

PHOSPHORUS FORMS AND RETENTION IN A SANDY SOIL RECEIVING DAIRY
WASTE EFFLUENT

By

ABDULLAH AL-SHANKITI

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2000

ACKNOWLEDGMENTS

Sincere appreciation and gratitude go to my major advisor, Dr. D. A. Graetz, for giving me all the help I needed throughout the course of my study. I would also like to thank my committee members-Dr. W. G. Harris, Dr. R. D. Rhue, and Dr. R. Nordstedt--for their guidance, comments, and suggestions. I am grateful to Dr. V. Nair for her insightful comments and suggestions, to Dr. K. R. Woodard for his help and support, and to D. Lucas for her encouragement and support.

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	viii
ABSTRACT	x
 CHAPTERS	
1 INTRODUCTION	1
Statement of the Problem	3
Objectives	4
Review of Literature	5
Soil Phosphorus	6
Phosphorus Accumulation	8
Phosphorus Forms and Fractionation	11
Phosphorus Retention	13
Downward P movement	20
Manure Management	22
Dissertation Format	23
 2 PHOSPHORUS ACCUMULATION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT	 25
Introduction	25
Materials and Methods	27
Experiment Location and Design	27
Soil Selection and Sampling	27
Soil Characterization	27
Effluent Application and Characterization	28
Statistical Analysis	28
Results and Discussion	30
Soil Properties Prior to Effluent Application	30
Effect of Application Rate and Cropping Systems	33
Summary and Conclusions	42

3	PHOSPHORUS FORMS AND FRACTIONATION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT	44
	Introduction.....	44
	Materials and Methods	46
	Experiment Location and Design	46
	Soil Selection and Sampling	46
	Fractionation Scheme	47
	Statistical Analysis.....	48
	Results and Discussion	48
	Study Site.....	54
	Summary and Conclusions	61
4	PHOSPHORUS RETENTION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT	63
	Introduction.....	63
	Materials and Methods	65
	Experiment Location and Design	65
	Soil Selection and Sampling	65
	Soil Characterization.....	65
	Calculations.....	67
	Statistical Analysis.....	68
	Results and Discussion	68
	Relative Phosphorus Adsorption (RPA)	68
	Degree of Phosphorus Saturation (DPS)	71
	Langmuir Adsorption Parameters.....	73
	Summary and Conclusions	77
5	DOWNWARD PHOSPHORUS MOVEMENT ASSESSMENT IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT	81
	Introduction.....	81
	Materials and Methods	83
	Experiment Location and Design	83
	Soil Selection and Sampling	83
	Soil Characterization.....	84
	Statistical Analysis.....	84
	Results and Discussion	85
	Summary and Conclusions	95
6	UTILIZATION OF DAIRY WASTE EFFLUENT THROUGH SEQUENTIAL CROPPING.....	97

Introduction.....	97
Materials and Methods	98
Experiment Location and Design.....	98
Sampling and Analysis	99
Results and discussion	100
Summary and Conclusions	105
 7 SUMMARY AND CONCLUSIONS.....	 108
 APPENDIX	
SELECTION OF SOIL: SOLUTION RATIO	114
LIST OF REFERENCES.....	118
BIOGRAPHICAL SKETCH	126

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2-1. Average annual concentrations (mg/L) of ammonium nitrogen ($\text{NH}_4\text{-N}$), total Kjeldahl nitrogen (TKN), soluble reactive P (SRP), and total P (TP) in effluent applied to the study site. Numbers in parentheses are standard deviations.....	28
Table 2-2. Selected characteristics of typical Kershaw sand (Soil Survey Staff, Gilchrist County, Florida, 1973) compared to the study site.	31
Table 2-3. Mehlich I-extractable elements concentrations and total P (TP) in "native" soil (n = 3 profiles) and study site (n = 12 profiles) soil profiles prior to beginning of the study.	32
Table 2-4. Statistical evaluation of TP data for the three-year study period.	34
Table 2-5. Regression equation relating Mehlich I-P to the independent variables Mehlich I-Ca, Mg, and Fe. (n=432).....	42
Table 3-1. P values (mg/kg) in each fraction within a soil depth increment at the beginning (1996) and end of the study period (1998) (n = 12 profiles). Values are Least Square Means (LSM).	49
Table 3-2. Percentage of P in each fraction within a soil depth increment at the beginning (1996) and end of the study period (1998)(n = 12 profiles). Values are Least Square Means (LSM).	50
Table 3-3. Increases in each fraction within a soil depth increment between the beginning (1996) and end of the study period (1998).	52
Table 3-4. Mean concentration of Mehlich I extractable elements (mg/kg) in the soil profile of the study site in 1996 prior to the application of effluent (n = 12 profiles).	54
Table 3-5. P values (mg/kg) in each of the fractions within a soil depth increment at the native site (n = 3 profiles). Values are Least Square Means (LSM).	55

Table 3-6. Percentage of P in each of the fractions within a soil depth increment at the native site (n = 3 profiles). Values are Least Square Means (LSM).....	55
Table 4-1. RPA values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native soil" (n = 1 profile). Values are Least Square Mean (LSM).	69
Table 4-2. Multiple regression equations relating RPA to a) Mehlich I (DA) Al, Fe and P, b) Oxalate Al, Fe, and P in 1996 (prior to the application of effluent) (n = 72). 72	
Table 4-3. DPS - 1 [†] % values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native" soil (n = 1 profile). Values are Least Square Means (LSM).	72
Table 4-4. DPS - 2 [†] % values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native" soil (n = 1 profile). Values are Least Square Means (LSM).	74
Table 4-5. Comparison of Langmuir parameters (S_{max} , EPC_0 , k) and S_0 mean values of different horizons within the soil profile prior to the application of effluent in 1996 and after two years of effluent application in 1998.....	76
Table 5-2. Mehlich I-extractable elements concentrations and total P (TP) in "native" soil (n = 1 profile) and study site soil profiles (n = 12 profiles) prior to the start of the study.	87
Table 5-3. Changes in WSP concentration within the soil profile under high application rate after the application of effluent (1998) vs. prior to the application of effluent (1996).	90
Table. 5-4. Changes in WSP concentration within the soil profile under the low application rate after the application of effluent (1998) vs. prior to the application of effluent (1996).	90
Table 6-1. P removed (kg/ha) by the corn-forage sorghum-rye cropping system under high and low application rates during the 1996-97 and 1997-98 seasons. (Data obtained from Woodard et al. 2000).	101
Table 6-2. P removed (kg/ha) by the perennial peanut-rye cropping system under high and low application rates during the 1996-97 and 1997-98 seasons. (Data obtained from Woodard et al. 2000).	103
Table 6-3. Average dry matter yield of the corn-forage sorghum-rye during the 1996-97 and 1997-98 seasons.	106
Table 6-4. Average dry matter yield of the perennial peanut-rye during the 1996-97 and 1997-98 seasons.	106

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 2-1. Average total P (TP) concentrations in the soil profile under the high rate application prior to application of effluent (1996) and after effluent application (1997 and 1998). Values are LSM± Std. Error.....	36
Figure 2-2. Average total P (TP) concentrations in the soil profile under the low rate application prior to application of effluent (1996) and after effluent application (1997 and 1998). Values are LSM± Std. Error.....	37
Figure 2-3. Mehlich I-extractable P concentrations in the soil profile prior to start of the study and after two years of effluent application (1998). Values are LSM± Std. Error.	38
Figure 2-4. Mehlich I-extractable P concentrations for cropping systems under the high rate effluent application in 1998. Values are LSM± Std. Error.....	40
Figure 2-5. Mehlich I-extractable P concentrations for cropping systems under the low rate effluent application in 1998. Values are LSM± Std. Error.....	41
Figure 3-1. Al-Fe-associated P (mg/kg) within the soil profile at the beginning 1996 and end of the study period (1998). Values are LSM± Std. Error.	51
Figure 3-2. Labile P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are LSM± Std. Error.	57
Figure 3-3. Ca-Mg associated P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are LSM± Std. Error.....	58
Figure 3-4. Residual-P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are LSM± Std. Error.	60
Figure 4-1. Relationship between Degree of P saturation (DPS - 1) calculated from oxalate extractable-P and Degree of P Saturation calculated from Mehlich I (DPS - 2) for soil samples from the study site.....	75

Figure 4-2. Relationship between Degree of P saturation calculated from oxalate extractable-P (DPS - 1) and equilibrium P concentration (EPC ₀) for soil samples from the study site.	78
Figure 4-3. Relationship between Degree of P saturation calculated from oxalate extractable-P (DPS - 1) and soluble P (P ₀) mg/L for soil samples from the study site.....	79
Figure 5-1. Mean water soluble P (WSP) concentrations within the soil profile of the study site under the high rate effluent application prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM± Std. Error.	88
Figure 5-2. Mean water soluble P (WSP) concentrations within the soil profile of the study site under the low rate effluent application prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM± Std. Error.	89
Figure 5-3. Mean water soluble P (WSP) concentration within the soil profile of the study site prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM± Std. Error.	92
Figure 5-4. Labile-P concentration within the soil profile of the study site prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM± Std. Error.....	93
Figure 6-1. P removal (kg/ha) of corn-forage sorghum-rye during the 1996-97 and 1997-98 seasons.	102
Figure 6-2. P removal (kg/ha) of perennial peanut-rye during the 1996-97 and 1997-98 seasons.....	104

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

PHOSPHORUS FORMS AND RETENTION IN A SANDY SOIL RECEIVING DAIRY
WASTE EFFLUENT

By

Abdullah Alshankiti

May 2000

Chairman: D.A. Graetz

Major Department: Soil and Water Science

Currently there are major concerns about the potential negative effects of nutrient losses from the waste of dairy farms on surface and ground water quality. In many confined livestock production systems, manures are normally applied at a rate designed to meet crop N requirements. However, this often results in a buildup of soil P above amounts required for optimal crop yield and increases the chances for P losses from source areas to water bodies.

This research, conducted at a dairy farm in north Florida, investigates the status of soil P under two main treatments of dairy waste effluent and two cropping systems. The N application rates were 448 and 896 kg/ha/yr which correspond to P loading of 112 and 224 kg/ha/yr. The cropping systems were perennial peanut-rye (P-R) and corn- forage sorghum-rye (C-FS-R). The objectives were to: (1) examine the accumulation of P in the soil profile, (2) quantify and characterize P forms in the soil profile, (3) quantify and

characterize P retention in the soil profile, (4) determine P uptake by the cropping systems, and (5) assess the downward movement of P.

The study site, mapped as Kershaw sand, appears to have been heavily loaded with animal waste (47 mg/kg Mehlich I-extractable P (MI-P) in the native area vs. 283 mg/kg in the study site surface soils). The MI-P increased significantly with high effluent rate application, particularly under the P-R cropping system, which suggests that the C-FS-R cropping system may be more effective in P removal than the P-R cropping system. Total P (TP) increased from 343 mg/kg in 1996 to 689 mg/kg in 1998. Water soluble P (WSP) increased but primarily in the lower depths of the soil profile under both treatments.

Al- and Fe-associated P constituted the major proportion (up to 60%) of the TP in the soil profile. Labile-P accounted for 18 to 30%, and Ca- and Mg-associated P accounted for about 10% of TP. Water soluble- and labile-P concentrations from 1996 and 1998 indicated a downward movement of P in the soil profile. These same data coincided with a decrease in retention capacity as determined by "Relative Phosphorus Adsorption" (RPA). Degree of P Saturation (DPS) data indicated that the surface horizon is more likely to release P than the deeper depths. The conclusions drawn from DPS were in agreement with the conclusions arrived at from the soil adsorption capacity and equilibrium phosphorus concentration (EPC_0).

Phosphorus removal was higher for the C-FS-R than for the P-R cropping system. The removal values agreed with published P uptake for such crops, but crop uptake did not alter the high level of soil P that was already present before application. When soil test P levels in the soil exceed optimum values for crop production, the application of

dairy waste based on estimated N requirement may not be appropriate on heavily P loaded sandy soil such as the soil at the study site.

CHAPTER 1 INTRODUCTION

The impact of current agriculture management practices in farmland or animal-related activity on water quality is well documented. Runoff from agricultural land is one of the major sources of nonpoint-source pollution. The USEPA has identified agriculture nonpoint-source pollution as the major source of stream and lake contamination that prevents attainment of water quality goals identified in the Clean Water Act (Parry, 1998; USEPA, 1996). The transport of phosphorus (P) to surface water can lead to accelerated eutrophication of these waters, which limit their use for fisheries, recreation, industry, or drinking. Although nitrogen (N) and carbon (C) are also associated with accelerated eutrophication, most attention has focused on P because P often limits eutrophication and its control is of prime importance in reducing the accelerated eutrophication of surface water (Thomann and Mueller, 1987)

Most P in agriculture soils is found either as insoluble precipitates of Ca, Fe and/or Al or as a constituent of a wide range of organic compounds. Water moving across or through soils removes both soluble P and sediments enriched with P, usually with the lighter, fine sized particles such as clays and organic matter. The soluble or particulate P then either can enter a flowing water body where it can be deposited as sediment or can be carried directly into a lake or pond. Phosphorus can also leach downward in the soil, perhaps to a tile drainage system or to ground water, where subsurface transport can then discharge the P into a stream or lake (Sharpley and Halvorson, 1994).

Most of the P that enters aquatic ecosystems comes from agricultural use. Phosphorus is added to lands as fertilizers, organic solids, wastewater, and feeds. It is estimated that 42,660 Mg of fertilizers was used during 1996 in Florida (Reddy et al., 1999). Fertilizer P is primarily in inorganic form, which is bioavailable and can be a major source of P for many ecosystems. For example, fertilizer P accounted for 51% of P imports to the Okeechobee Basin (Bogges et al., 1995). Another significant source of P input to the lake was the dairy farming and beef cattle ranching north of the lake which accounted for about 49% of the TP input to the lake (Federico et al., 1981). Thus, optimal dairy waste management practices are more necessary than ever; more cows on limited land area increase the likelihood of environmental problems resulting from mismanagement of dairy farm wastes. A dairy waste management system should account for the fate of nutrients that may be of environmental concern. The overall goal of sound agronomic and environmental management programs for soil P is to maximize plant growth, while minimizing losses of P to surface waters (Lanyon, 1994). It is important, therefore, to understand the role of soil reactions in controlling the availability of soil P for plant uptake or loss in erosion, surface runoff, and leaching. Amounts of P exported from watersheds are tied to watershed hydrology, soil P content, and amount of P added as fertilizer or manure. This assumes in most cases that P export from watersheds occurs in surface rather than subsurface runoff, although it is recognized that in some regions of the US dominated by sandy or organic soils P can be transported in subsurface drainage waters. Generally, the P concentration in water moving through the soil profile is small due to sorption of P, except in acid organic or peaty soils where the adsorption affinity and capacity for P retention are low (Sims et al., 1998). Similarly, sandy soils with low P

sorption capacities, waterlogged soils, and soils with preferential flow through macropores and earthworm holes are susceptible to P movement (Sharpley and Syers, 1979).

Statement of the Problem

In 1990, the Middle Suwannee River area was approved as a Hydrologic Unit Area project based on data generated by the Florida Department of Environmental Protection. These data showed an elevated concentration of nitrate-nitrogen in the Floridan Aquifer in the Suwannee River Basin, especially in areas of intensive agricultural activity. Phosphorus concentrations in the Suwannee River ranged from 0.40 to 0.49 mg/L which were 6.4 times the median regional value of north Florida streams. The Hydrologic Unit Area program was developed to reduce or prevent water quality degradation of the Floridan Aquifer and the Suwannee River resulting from agricultural operations. Management of nutrients (potential contaminants) in dairy waste effluent through spray field crop production systems is an important component in the overall scheme for protecting ground and surface water from elevated levels of N and P. The use of inappropriate crop management technology under a dairy effluent irrigation system can lead to the loss of N to the ground water. Uptake of nutrients by agronomic crops sequenced over time is an effective, economical, and environmentally sound means of nutrient recovery. Cropping systems designs are needed to meet environmental demands by maximizing nutrient uptake while meeting the needs of dairy producers.

The Use of Dairy Manure Effluent in A Rhizoma (Perennial) Peanut Based Cropping Systems for Nutrient Recovery and Water Quality Enhancement is a research project established under the Hydrologic Unit Area project (HUA). The objective of this

project was to evaluate five cropping systems grown under a dairy effluent disposal irrigation system, comparing their effectiveness in nutrient recovery and maintenance of acceptable levels of N and P in ground water. The cropping systems were corn-forage sorghum-rye, corn-bermudagrass-rye, bermudagrass-rye, perennial peanut-rye, and corn-perennial peanut-rye. The N application rates were 448, 672 and 896 kg/ha/yr which correspond to P loadings of 112, 168 and 224 kg/ha/yr. My study was a component of this project and addressed P forms and retention in the soil profile under two cropping systems (corn-forage sorghum-rye and perennial peanut-rye) and two N application rates (448 and 896 kg/ha/yr) which correspond to P loadings of 112 and 224 kg/ha/yr.

In order to achieve the objectives mentioned below, two cropping systems were chosen from the main study: corn-forage sorghum-rye and perennial peanut-rye. The workload associated with evaluating each treatment in the overall project would have been prohibitive, therefore treatments were selected which provide representative data with regard to the fate of P in the various cropping systems. The former is commonly used by North Florida dairies (Staples, 1997). Recently, perennial peanut has been identified as promising for its potential of continuous nutrient recovery over an extended period of the year and for production of high quality forage

Objectives

The main objective of this research was to study the effect of dairy waste effluent application on P accumulation, forms, and retention in the soil profile of a sandy soil under two cropping systems. The cropping systems were corn-forage sorghum-rye, which represent the traditional crops for the Middle Suwannee River area, and perennial peanut-

rye, an improved cropping system to be introduced to the area. The specific objectives and hypotheses of this research were as follows:

Objective 1: Quantify and characterize inorganic P forms in the soil profile of the chosen cropping systems with increasing effluent P application.

Hypothesis: Application of dairy waste effluent will increase P levels in the soil resulting in an accumulation of P in the soil profile.

Objective 2: Quantify and characterize P retention capacity in the soil profile.

Hypothesis: Soil retention capacity will decrease with continuous addition of dairy waste effluent and may induce a downward movement of P.

Objective 3: Determine P uptake by the chosen cropping systems under two rates of effluent application.

Hypothesis: P accumulation in soil profile will decrease with increasing plant uptake.

Review of Literature

Phosphorus (P) is an integral and essential part of the food production system, but P doesn't occur abundantly in most soils. Total P concentration in surface soils varies between about 0.02 and 0.10% (Tisdale et al., 1993). The native P compounds are mostly unavailable for plant uptake, some being highly insoluble. When soluble sources of (P) as those in fertilizer and manure are added to soils, they are fixed or are changed to unavailable forms and in time, react further to become highly insoluble forms. Farmers commonly apply more P in fertilizers and manure than is removed by the crops. In time, soil P levels increase often to high enough levels to reduce significantly future

requirements for P fertilizers and cause a buildup of P reserves in the soil profile (Brady, 1990).

Soil Phosphorus

Phosphorus in agriculture soils is found in inorganic and organic forms. Inorganic forms represent 50-70% of soil P, although this fraction can vary from 10 to 90% (Pierzynski et al., 1994). Inorganic forms are typically hydrous sesquioxides and insoluble precipitates of Ca, Fe and/or Al. Organic P varies between 15 and 80% in most soils (Tisdale et al., 1993). The quantity of organic P in soil generally increases with increasing C and /or N. Many of the organic P compounds in soils have not been characterized, but most are esters of orthophosphoric acid and have been identified primarily as inositol phosphate, phospholipids, and nucleic acids. Organic P turnover in soils is a result of P mineralization and immobilization reactions which, in general, are similar to those of N as both processes occur simultaneously in soils. The initial source of soil organic P is plant and animal residue, which is degraded through microbial activity to produce other organic compounds and release inorganic P (Tisdale et al., 1993).

There is an interrelationship between the various forms of P in soils. The decrease in soil solution P concentration with absorption by plant roots is buffered by both inorganic and organic fractions in soil. Primary and secondary P minerals (nonlabile P) dissolve to resupply $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ in solution. Inorganic P adsorbed on mineral and clay surfaces as H_2PO_4^- or HPO_4^{2-} (labile inorganic P) also can desorb to buffer P in solution P.

Numerous soil microorganisms digest plant residues containing P and produce many organic P compounds in soil. These organic P compounds can be mineralized through microbial activity to supply inorganic P. Soil solution P is often called the

'intensity factor', while the inorganic adsorbed P and organic labile P fractions are collectively called the 'quantity factor'. Maintenance of solution P concentration or (intensity) for adequate P nutrition in the plant depends on the ability of labile P (quantity) to replace soil solution P taken up by the plant. The ratio of quantity to intensity is called the 'capacity factor' which expresses the relative ability of the soil to buffer changes in soil solution P. Generally, the larger the capacity factor, the greater the ability to buffer solution P. The P cycle can be simplified to the following relationship:

Soil solution \leftarrow ----- \rightarrow Labile P \leftarrow ----- \rightarrow nonlabile P

Labile P is the readily available portion of the quantity factor that exhibits a high dissociation rate and rapidly replenishes solution P. Depletion of labile P causes some nonlabile P to become labile, but at a slow rate. Thus, the quantity factor comprises both labile and nonlabile fraction (Tisdale et al., 1993).

The division of P in the soil's solid phase into the labile and nonlabile forms comes about from a kinetic consideration. From a mechanistic point of view, P in the soil's solid phase can be classified by yet another way into adsorbed P and crystalline P. The first refers to P adsorbed on active surfaces in the soil, and the second to distinct P compounds either formed as reaction products, or inherently present in the soil matrix. The two types of categorization (i.e., labile vs. nonlabile and adsorbed vs. crystalline) are not synonymous, although a great deal of overlap exists between the two. The labile P does not represent a precisely distinct phase of solid phase P, but one that has arbitrary boundaries of time and other procedural factors. Any loss of precision in defining labile P is paralleled by an equal uncertainty in defining the remaining P (Olsen and Khasawneh, 1980). Phosphorus amendments, in either organic or inorganic form, are needed to

maintain adequate available soil P for plant uptake. Once applied, P is either taken up by the crop or becomes weakly or strongly adsorbed onto Al, Fe and Ca surfaces. With the application of P, available soil P content increases as a function of certain physical and chemical soil properties, such as clay, organic C, Fe, Al and calcium carbonate content. The continual application of P can result in an increase in soil test P above levels required for crop uptake, which has an environmental ramifications.

Phosphorus Accumulation

In many parts of the world, concern and research focuses on manure application, where the amount of P added often exceeds crop removal rate on an annual basis. Many areas with intensive confined animal operations, such as the Netherlands, Belgium, north-eastern USA and Florida, now have soil P levels that are of environmental rather than agronomic concern (Sharpley et al., 1994b). In 1994, Kingery et al. (1994) reported P leaching to a depth of ~60 cm in tall fescue pastures in the Sand Mountain region of northern Alabama that had received long term-application (15-28 yr) of poultry litter. Soil test P (Mehlich I) values in topsoils were extremely high (~230 mg/kg) relative to optimum values for crop production in this region (25 mg/kg) (Cope et al., 1981). Similarly, Eghball et al. (1996) measured soil test P (Olsen P) in the profile of a Tripp very fine sandy loam (a coarse-silty, mixed, mesic Aridic Haplustoll) that had received long-term (>50 yr) application of cattle feedlot manure and/or fertilizer P. Crops grown included sugarbeet, potato, and corn. Increases in soil test P were reported and the increases were associated with P leaching to ~75 cm with fertilizer P (superphosphate) and to ~1.0 m for manure or manure plus fertilizer P. Mozaffari and Sims (1994) measured soil test P (Mehlich I) values with depth in cultivated and wooded soils on farms on a coastal plains watershed dominated by intensive poultry production and

frequent applications of poultry litter, and observed P leaching to depth of ~60 to 75 cm in agricultural fields and a high soil test P values in topsoils relative to those considered optimum for most agronomic crops (25 mg/Kg) (Sims and Gartley, 1996). In North Carolina, King et al. (1990) examined the effect of 11 years of swine lagoon effluent application on P distribution within the profile of a Paleudult soil used for coastal bermuda grass pasture, and reported soil test P (Mehlich I) values much greater than required for crop production (225-450 mg/kg as a function of effluent rate, vs. an optimum soil test value of ~20-25 mg/kg). Soil test P at the 15 to 30, 30 to 45, 45 to 60, and 60 to 75 cm depths was <5 mg/kg in nearby unfertilized pasture. However, at the same depths, soil test P was about 120, 75, 25, and 5 mg/kg at the lowest effluent rate (335 kg N/ha per year) and 350, 175, 125, and 50 mg/kg at the highest effluent rate (1340 kg N/ha per year).

The same trend of P accumulation and leaching has also been shown in Florida which has intensive agricultural activity, humid climate, frequent heavy rainfall, and widespread use of irrigation and drainage. Several studies have shown the extent of P leaching that can occur in deep, sandy soils. For example, a study by Wang et al. (1995) found that high levels of P could be leached from surface (Ap) horizons of four sandy Florida soils heavily loaded with dairy manure despite high pH and abundant Ca^{2+} in solid and solution phases. Total P (TP) ranged from 3144 to 1595 mg/kg. Further investigation on the composition of the same samples by Harris et al. (1994) showed that the dominance of noncrystalline Si and lack of crystalline Ca-P in the intensive area Ap horizons constitute an unfavorable environment for P retention in these soils. The crystallization of Ca-P may be inhibited by manure-derived component such as Mg,

organic acids, and Si. Nair et al. (1995) also studied the forms of P in soil profiles from dairies of south Florida. The dairies selected were active (still operating at the time of sampling) and abandoned (dairies that had not been operating for 4, 12, 18 yr prior to sampling). Three components of each active dairy were sampled: intensive areas (areas next to the barn where cattle are held immediately prior to milking), pasture (areas used for grazing), and forage areas (used for forage production). Their result showed a TP for the A horizon ranging from 3028 mg/kg for the active-intensive areas to 2933 mg/kg for the abandoned-intensive areas. Total P content of the unimpacted soils (native) was in the range of 15-59 mg/ kg for all horizons, with low values observed in the E horizon and high values in the Bh horizon. Labile P content (defined as P in sorbed phase, which is potentially mobile and bioavailable) in the Bh horizon of native forage and pasture areas were less than 2% of the TP, while up to 10% of TP was found as labile P in surface horizons. In intensive areas, up to 40% of the P was in the labile pool. Soil P content varied both with soil depth and land use. Total P stored in the soil profile increased with intensity of land use, with native unimpacted areas containing 44 g P m⁻² (average profile depth 99 cm), followed by forage (46 g P m⁻²; soil depth 94 cm) pasture (102 g P m⁻²; soil depth 119 cm) and intensive areas (766g P m⁻²; soil depth 136 cm). Dairy lagoon effluent, though its composition and P content is quite different from dairy manure could also elevate the level of P in the soil. Dooley (1996) studied P accumulation and retention in a wetland impacted by approximately 20 years of dairy lagoon effluent application and showed that the wetland appeared to be exporting P to an adjacent stream. His study concluded that in order to accomplish acceptable levels of treatment, the assimilative capacity of the wetland must be considered.

Numerous studies on accumulation of P in soils amended with commercial fertilizers and /or organic wastes, including some of the above-mentioned studies, have been reviewed recently by Sims et al. (1998). He indicated clearly that the most common agricultural situation associated with significant downward movement of P has been the accumulation of P to “very high” or “excessive” levels in soils from continuous application of organic wastes (manure, litter, and municipal or industrial wastes and waste waters).

Phosphorus Forms and Fractionation

In order to understand the potential for P transport, P forms have to be examined and evaluated to develop an understanding of the stability of P in the soil of the area adjacent to the water body. The objectives of P fractionation in general are to provide insight into the fate and transformation of P added to soils as fertilizers or manure, estimate the availability of P to plants for agronomic purposes, estimate the potential for P movement from erosion and through leaching, and provide information regarding the interaction between P in sediments and the overlaying water in the case of aquatic systems (Graetz and Nair, 1999). Fractionation schemes using various chemical extracts have been developed through the years to quantify the different forms of P in soils. The underlying assumption here is that inorganic P in soil consists of varying proportions of three discrete classes of compounds, namely, phosphates of Fe, Al and Ca, some of which could be occluded or enclosed within coatings of Fe oxides and hydrated oxides. These chemical P forms are operationally defined and subject to broad interpretations. Nevertheless, they offer a convenient means for obtaining significant information on P chemistry of soils. For example, through a modification of Hieltjes and Lijklema (1980) fractionation method Nair et al. (1995) examined soil phosphorus in soil from dairies of

south Florida and fractionated it into labile P, inorganic Fe/Al-P, Ca/Mg-P and residual-P. This fractionation scheme offered significant information on the forms of P in soil profiles from dairies of south Florida. The Hietjies & Lijkema (1980) scheme uses 1 M NH_4Cl to extract loosely bound and labile P. This fraction is believed to contain the water soluble portion and the plant- available portion of TP in the sample. Sodium hydroxide is the next step in the fractionation procedure. This extract contains both organic and inorganic P forms. The inorganic P portion of the extract is believed to be associated with Fe and Al, while the organic portion is believed to be fulvic-and humic bound. Hydrochloric acid is the third step to remove calcium-bound phosphate. The remaining soil can then be digested to measure any residual P. This portion of P is considered to be highly resistant, organically bound.

The forms of P in soil profiles from dairies of south Florida illustrate the fate and transport of P in these systems Nair et al. (1995). They identified the P forms in the soil profile of differentially manure-impacted soils in the Okeechobee watershed of south Florida. All soils were Spodosols, and soils were collected by horizon, A, E, Bh, and Bw. Their results showed no statistical differences in the percentage of labile P (NH_4Cl -extractable P), the P that would most likely move from A horizon of the various components. More P will be lost from the heavily manure-impacted intensive areas with high TP values, than from the less impacted pasture, forage and native areas. They also observed that the P would continue to be lost from dairies that have been abandoned for considerable period of time. The P that leaves the surface horizon might be lost through surface and subsurface drainage, and the portion that reaches the spodic (Bh) horizon will be held as Al- and Fe-associated P, either in the inorganic or in the organic fraction. The

high percentage of HCl-extractable P (Ca- and Mg-associated P) in the A horizon of the intensive dairy component was also of potential concern. This P could be continuously extracted by NH_4Cl or by water (Graetz and Nair, 1995), suggesting that about 80% of the total soil P had the potential to move eventually with drainage water into Lake Okeechobee.

Fractionation of P forms has been particularly useful in understanding the transformation of P added to soil, either in inorganic or organic amendments such as manures. Zhang and Mackenzie (1997) used P fractionation and path analysis to compare the behavior of fertilizer and manure-P in soils. Their results showed that P behaves differently when added as manure, compared to inorganic fertilizer, which may affect the depth of P movement through the soil profile. Simard et al. (1995) reported that a significant portion of the P moving downward in soils receiving substantial amounts of animal manure accumulated in labile forms such as water-soluble, Mehlich-3, and NaHCO_3 extractable P forms. Eghball et al. (1996) found that P from manure moved deeper in the soil than P from chemical fertilizer in long term (>50 yr) studies.

Phosphorus Retention

P retention in soils is a result of many soil physical and chemical properties, such as mineralogy, clay content, pH and organic matter content, that influence the P solubility and adsorption reactions. Consequently, these soil properties also affect solution P concentration, P availability and recovery of P fertilizer by crop (Tisdale et al., 1993). The term frequently used to describe surface adsorption and precipitation reactions collectively is P fixation or retention. The term adsorption and chemisorption also have been used to describe P reaction with mineral surfaces, where chemisorption generally represents a greater degree of bonding to the mineral surface. The term sorption has been

used to describe adsorption and chemisorption collectively. Adsorption is the preferred term (Tisdale et al., 1993). There is considerable evidence suggesting that, P retention is a continuous sequence of precipitation and adsorption. With low-solution P concentration, adsorption probably dominates, while precipitation reaction proceed when the concentration of P and associated cations in the soil solution exceeds that of the solubility product (K_{sp}) of the mineral. Mineral solubility represents the concentration of ions contained in the mineral that is maintained in solution. Each P mineral will support a specific ion concentration which depends on the solubility product of the mineral. The most common P minerals found in acid soil are Al-and Fe-P minerals, while Ca-P minerals predominate in neutral and calcareous soils. But, the specific P minerals present in the soil and the concentration of solution P supported by these minerals are highly dependent on solution pH (Tisdale et al., 1993).

Phosphorus sorption may be determined by single point adsorption isotherm or multi-point adsorption isotherms and can be described by several different adsorption equations; all are based on the fundamental equation:

$$q = f(C)$$

where q is the quantity of P adsorbed at P concentration C .

One of the earliest equations used in soil studies is the Freundlich equation,

$$q = ac^b$$

The amount of P adsorbed per unit weight of soil is q , c is the P concentration in solution, and a and b are constant which vary from soil to soil. The Freundlich equation was introduced as a purely empirical equation. It implies that the energy of adsorption decrease exponentially with increasing saturation of the surface. However, no maximum

capacity of adsorption can be calculated because the amount of adsorption increases with the adsorbing ions in the solution (Yuan and Lucas, 1982). Therefore, it applies well only over a limited concentration range of ions to be adsorbed. For this reason, the Langmuir equation, which is based on the assumption that adsorption is on localized sites, the energy of adsorption is constant, and the maximum adsorption possible corresponds to a complete monomolecular layer is often preferred for the description of soil P adsorption. In its linear form, the regression line would provide a means to calculate not only the maximum adsorption but also a constant which is assumed to be related to the bonding energy of the surface for P in solution. The equation describes a finite limit to adsorption so that a maximum value may be obtained (Yuan and Lucas, 1982). Although there are several linear forms, they are all derived from the basic expression:

$$q = kbc/(1+kc)$$

where q and c are as in the Freundlich equation, b is the "P adsorption maximum", and k is a constant related to bonding energy.

The Temkin equation, as proposed for use in soil-P system by Bache and Williams (1971), also implies that the energy of adsorption decreases as the amount of P sorbed increases. In the middle range of P sorption, the equation may be expressed as

$$q/b = (RT/B)\ln Ac$$

where A and B are constant and b , c and q are as in the Langmuir equation. All three equations require that equilibrium conditions exist, a state that is rarely achieved in soil-P adsorption studies. Another assumption common to the three equations is that the adsorption is reversible; however some portion of the P adsorbed by soil is irreversibly adsorbed. Despite these and other disadvantages, the three equations have been useful in

describing the relationship between c and q over limited range of concentrations (Olsen and Khasawneh, 1980).

In Florida, the P retention characteristics of upland and wetland soils and stream sediment in the Lake Okeechobee Watershed (maximum P retention capacity [S_{\max}] and equilibrium P concentration [EPC_0]) have been a point of interest for several studies (Reddy et al., 1996). The S_{\max} of Bh horizons was about three to four times higher than the surface A and E horizons. High EPC_0 (equilibrium concentration when net adsorption equal zero) values for soils in the A and E horizons suggest poor retention capacity, while low EPC_0 values of the Bh horizon indicate strong affinity for P. The S_{\max} was found to be highly correlated with oxalate-extractable Fe and Al, and total carbonate of the soil. Oxalate-extractable Fe and Al represent amorphous and poorly crystalline forms. Many soils effectively retain P due to the presence of mineral components with high surface affinity for orthophosphate. However, movement of P from dairy farms to aquatic systems does occur under certain conditions, and has been linked to eutrophication of surface water. This movement may be related to erosion or to subsurface transport. Subsurface transport of P can be significant in sandy soils due a paucity of P-retaining components (Reddy et al., 1996).

Sandy soils generally retain less P than finer textured soils because of a deficiency of mineral components having surface affinity for orthophosphate. In a 1982 study by Yuan and Lucas pertaining to the retention of phosphate by thirty Florida sandy soil as evaluated by adsorption isotherms showed that the simple linear Freundlich equation describe the P adsorption properties of sandy soil more successfully than the Langmuir equation. The adsorption maximum values obtained from the Freundlich equation were

correlated with soil properties. A significant relationship was found with clay content but not with double acid extractable Al, Fe, Ca and Mg, individually or combined. However, for soils with a pH below 5.5, the adsorption maximum had a significant relationship with extractable Al. A study on P retention as related to morphology and taxonomy of sandy coastal plain soil materials by Harris et al (1996) distinguished between two groups of uncoated Quartzipsamments (< 5% silt-plus-clay); those having "clean" (coating-free) and "slightly-coated" grains. All clean samples readily desorbed P regardless of origin or amount adsorbed. Sand-grain coatings significantly enhanced P adsorption and resistance to desorption. Thus, clean sands pose a greater hazard for P leaching than sands with grain coatings. Clay content was closely related to P adsorption, but silt content was not. The P-retention distinction between clean and other Quartzipsamments is more marked than uncoated vs. coated family criterion. The distinction between clean and other sandy materials was more discrete and consistent for P desorption behavior than for adsorption. A P-adsorption measurement such as the RPA (Rapid Chemical Assessment of Relative Phosphorus Adsorption [single-point isotherm]) would provide a reasonably valid assessment of P retention for slightly-coated and coated sand materials if appropriately calibrated. The RPA effectively arrayed sandy Florida soil samples with respect to relative P adsorption. A single-point isotherm could effectively index these sandy materials. It does not directly provide values for maximum P adsorption, but it closely relates to such values derived from P adsorption isotherm for the same sandy soil studied (Harris et al., 1996).

A recent study by Nair et al. (1998) conducted on Spodosols in the Lake Okeechobee basin to evaluate the P retention capacity of manure impacted Bh horizons

under aerobic and anaerobic conditions found that a high watertable decreased the P retention for the majority of the soils in that study. High manure-impacted areas have Bh horizons with high P concentrations as a result of P movement from the surface A horizon through the eluted E horizon. The P appeared to be temporarily retained and could be released upon prolonged contact with water. Another study by Nair et al. (1999) of Spodosols in the same basin showed that the surface A and E horizons of manure-impacted soils had essentially no sorbing capacity while the Bh (spodic) and Bw horizons had mean S_{\max} values 430 and 385 mg/kg, respectively. The P retention characteristics of these soils were determined by using both single-point (1000 mg P/kg or 100 mg P/L) and traditional Langmuir isotherms. Phosphorus sorption values using a single high P solution had approximately a 1:1 relationship with values obtained for the maximum retention capacity (S_{\max}) obtained from Langmuir isotherms.

In response to the fact that the P sorption capacity of soils is not unlimited, and based on documented accumulation and leaching of P in soils of areas dominated by concentrated animal production, a new approach to sorption capacity was developed. The concept of Degree of P Saturation (DPS) is based on the fact that the potential for soil-P desorption increases as sorbed P accumulates in soil (Van der Zee et al., 1987; Breeuwsma and Silva, 1992). Degree of P saturation is defined as the ratio of extractable P to the sum of extractable Fe and Al expressed as an percentage. The critical DPS threshold has been defined as the saturation percentage that should not be exceeded to prevent adverse effect on ground water quality with the specific goal that the phosphate concentration in the ground water should not exceed 0.01 mg/L of orthophosphate at the level of the mean high watertable (Breeuwsma et al., 1995). A critical DPS value of 25%

has been used in the Netherlands to determine the surplus of P that can be applied to varying soil types before P saturation, and thus significant P export in subsurface runoff, can be expected to occur.

Operationally, DPS is defined as oxalate-extractable P divided by the phosphate sorption capacity of the soil that is estimated from equations including oxalate-extractable Fe and Al (Breeuwsma et al., 1995).

$$\text{DPS} = \frac{\text{Extractable soil P}}{\text{P sorption maximum}} \times 100$$

The extractable P (P_{ox}) is determined by extraction by 0.2 M ammonium oxalate buffered to pH 3.0. Phosphorus sorption capacity is determined by standard P adsorption isotherms or estimated by oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}) and the DPS expressed as:

$$\text{DPS} = \frac{P_{\text{ox}}}{\alpha (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})} \times 100$$

The saturation factor α , as defined by Sjoerd et al. (1988), is the ratio of the amount of P that is sorbed in laboratory experiments and the P already present as P_{ox} to ($\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$). Thus α is a variable that allows comparison of different soils with respect to P saturation, and the result will then be normalized with respect to the reactive soil constituents. However, as pointed out by Sjoerd et al. (1988), the proportionality factor α is both concentration and time dependent. Pautler and Sims (1998) used an α value ranging from 0.4-0.6 for soils of the Atlantic coastal plain.

An added advantage of the DPS approach is that it not only describes the potential for P release from soil but also indicates how close the P-sorption sites of a soil are to being saturated (Sibbesen and Sharpley, 1997). Citing data from numerous studies in the Netherlands, showed that more than 80% of the soils in a watershed with intensive livestock production were saturated with P (Breeuwsma et al., 1995). During winter months, when groundwater discharge to surface waters was highest, concentration of TP in the shallow groundwater to exceeded surface water quality standards (0.15 mg/L of TP). Lookman et al. (1995) applied the DPS approach to a 700 Km² area (primarily grassland used for intensified animal agriculture) in northern Belgium. Based on a critical DPS value of 25%, they estimated that >75% of the soils were considered to be saturated with P to the depth of the highest average groundwater table. Lookman et al. (1996) showed that the DPS of the same soils of their 1995 study (Lookman et al., 1995) at the 0-30 cm depth was highly correlated with soluble P in these soils. Sharpley (1995) also found a single relationship (r^2 of 0.86) describing the concentration of dissolved phosphate (DP) as a function of P-sorption saturation for ten soils ranging from sandy loam to clay in texture. He used Mehlich-3 as extractable soil P and the Langmuir P-sorption maximum as P-sorption capacity in his calculation of P-sorption saturation. Comparison of short-and long-term sorption kinetics in Atlantic coastal plain soils showed that the potential for P loss from over-fertilized soils can be improved by a knowledge of the degree of P saturation of the soils (Pautler and Sims, 1998).

Downward P movement

Loss of P from land can occur in three ways; as water-soluble and/or particulate P in surface runoff, as water-soluble and/or particulate P in subsurface runoff (leaching), and as water-soluble and/or particulate P in flow to groundwater, referring to P picked up

by water that passes to the water-table and which is subsequently discharged to streams, rivers or lakes as seepage (Ryden et al., 1973). Phosphorus leaching has normally been considered to be inconsequential in most soils, but recent studies show that there are combinations of agriculture management practices, soil properties, and climatic conditions that can result in significant accumulation in subsoils. Whether or not P that leaches into subsurface horizons is later transported to water bodies depends on the depth of leaching and the hydrological connections of the watershed (Sims et al., 1998). As mentioned above in the section on P accumulation, numerous studies on accumulation of P in soils amended with commercial fertilizers and/or organic wastes have been reviewed recently by Sims et al., (1998). This indicated clearly that the most common agricultural situation associated with significant downward movement of P has been the accumulation of P to "very high" or "excessive" levels in soils from continuous application of organic wastes (manure, litter, and municipal or industrial wastes and waste waters). Studies by Kingery et al. (1994), Eghball et al. (1996), Mozaffari and Sims (1994), and King et al. (1990) report P leaching to ~75 cm depending upon other factors such as soil type and P accumulated in the surface horizon. Furthermore, Eghball et al. (1996) suggested a greater downward mobility for organic forms of P. Previous studies from Florida also illustrated the extent of P leaching that can occur in deep, sandy soils. One of the earliest studies in Florida was of Bryan (1933) who reported P leaching to depths of at least 90 cm in heavily fertilized citrus groves of varying ages. Humpherys and Pritchett (1971), in their study of six soil series in northern Florida, 6 to 10 years after applying superphosphate, reported extensive P leaching and subsequent accumulation in the spodic horizon of a Leon fine sand and that all fertilizer P had leached below a depth of 50 cm in

Pomello and Myakka soil series. A study by Wang et al. (1994) found that high levels of P could be leached from surface (Ap) horizons of four sandy Florida soils heavily loaded with dairy manure despite high pH and abundant Ca^{2+} in solid and solution phases.

Graetz and Nair (1995), Nair et al. (1995), Nair et al. (1998), and Nair et al. (1999), in a series of studies on Spodosols in the Lake Okeechobee basin of Florida, concluded that P that leaves the surface (A) horizon might be lost through surface and subsurface drainage, and the portion that reaches the spodic (Bh) horizon will be held as Al- and Fe-associated P, either in the inorganic or in the organic fraction. The high percentage of HCl-extractable P (Ca- and Mg-associated P) in the A horizon of the intensive dairy component was also of potential concern. This P could be continuously extracted by NH_4Cl or by water, suggesting that about 80% of the total soil P had the potential to move eventually with drainage water into Lake Okeechobee (Graetz and Nair, 1995).

Recently, Sims et al. (1998) reviewed some current research on P leaching and loss in subsurface runoff in Delaware, Indiana, and Quebec and concluded that the situation most commonly associated with extensive P leaching, and thus the increased potential for P loss via subsurface runoff, has been the long-term use of animal manures.

Manure Management

Developing manure management plans that are agronomically, economically, and environmentally sound is a challenge because issues like accelerated eutrophication, P or N limitation, transport mechanisms, source management, soil P level, environmental soil testing for P, manure management and land application of manure have to be considered. This review of the literature shows the urgent need for research especially in areas of intensified dairy production and deep, coated sandy soil. Many factors can be involved in developing an environmentally sound plan for manure management. Animal manure can

be a valuable resource if it can be integrated in cost effective best management practices. Uptake of nutrients by agronomic crop sequenced over time is an effective, economical, and environmentally sound means of nutrient recovery, especially if the cropping system met the environmental concerns. The environmental concerns can be met by maximizing nutrient uptake by the crops while meeting the need of dairy producers.

A recent two years study on the use of dairy manure effluent in a rhizoma (perennial) peanut based cropping system (French et. al. 1995) suggests that, if N pollution is the major concern in a particular area, then the PP-R cropping system (year-round perennial peanut and rye) would be a good choice since it performed as well or better than the C-FS-R (corn, forage sorghum, and winter rye) and C-PP-R (corn planted into a perennial peanut sod, perennial peanut, and rye) systems. However, if P is the major concern, the C-FS-R and C-PP-R systems would be better choices. The C-FS-R and C-PP-R systems were superior to the PP-R rotation in P removal values. Though P level in perennial peanut forage were generally higher than those in corn and forage sorghum, they were not high enough to compensate for the much lower annual dry matter yield of the perennial peanut system.

Dissertation Format

The subsequent chapters in this dissertation were prepared as individual manuscripts. In this chapter, a general introduction, statement of the problem, review of literature, and research objectives were presented. In chapter 2, the accumulation of P in a sandy soil receiving dairy waste effluent was investigated. In chapter 3, the forms and fractionation of P in the area under study were examined. In chapter 4, the retention capacity of the soil was evaluated. In chapter 5, downward P movement was examined.

In chapter 6, plant uptake of the cropping systems under study was investigated. Chapter 7 provides a summary and conclusion of results presented in previous chapters.

CHAPTER 2

PHOSPHORUS ACCUMULATION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT

Introduction

The number of soils with plant-available P exceeding the levels required for optimum crop yield has increased in areas of intensive agriculture and livestock production (Sims, 1992; Snyder et al., 1993). In many parts of the world, concern and research focuses on manure application, where amounts of P added often exceeded crop removal rate on an annual basis. Many areas with intensive confined animal operations, such as the Netherlands, Belgium, north-eastern USA and Florida, now have soil P levels that are of environmental rather than agronomic concern (Sharpley et al., 1994b). In 1994, Kingery et al. (1994) reported P leaching to a depth of ~60 cm in tall fescue pastures in the Sand Mountain region of northern Alabama that had received long term-application (15-28 yr) of poultry litter. Soil test P (STP) (Mehlich I) values in topsoils were extremely high (~230 mg/kg) relative to optimum values for crop production in this region (25 mg/kg) (Cope et al., 1981). Similarly, Eghball et al. (1996) measured STP (Olsen P) in the profile of a Tripp very fine sandy loam (a coarse-silty, mixed, mesic Aridic Haplustoll) that had received long-term (>50 yr) application of cattle feedlot manure and/or fertilizer P. Crops grown included sugarbeet, potato, and corn. Increases in STP were reported and the increases were associated with P leaching to ~75 cm with fertilizer P (superphosphate) and to ~1.0 m for manure or manure plus fertilizer P. Mozaffari and Sims (1994) measured STP (Mehlich I) values with depth in cultivated and

wooded soils on farms in a coastal plains watershed dominated by intensive poultry production and frequent applications of poultry litter, and observed P leaching to depth of ~60 to 75 cm in agricultural fields. STP (Mehlich I) values in these soils were very high in topsoils relative to those considered optimum for most agronomic crops (25 mg/kg) (Sims and Gartley, 1996). In North Carolina, King et al. (1990) examined the effect of 11 years of swine lagoon effluent application on P distribution within the profile of a Paleudult used for coastal bermudagrass pasture. They reported STP (Mehlich I) values much greater than required for crop production 225-450 mg/kg vs. an optimum soil test value of ~20-25 mg/kg. Soil test P at the 15 to 30, 30 to 45, 45 to 60, and 60 to 75 cm depths was <5 mg/kg in nearby unfertilized pasture. However at the same depths, STP was about 120, 75, 25, and 5 mg/kg at the lowest effluent rate (335 kg N/ha per year) and 350, 175, 125, and 50 mg/kg at the highest effluent rate (1340 kg N/ha per year). Phosphorus loading from dairy lagoon effluent to soils in the Lake Okeechobee Basin, Florida resulted in significant accumulation of P. In some cases, P concentrations were about 50 times that of unimpacted areas (Graetz and Nair, 1995).

A considerable body of research now shows that STP levels influence the amount of P in runoff water and subsurface drainage (Pote et al., 1996 ; Sharpley et al., 1977; Heckrath et al., 1995). Therefore, STP could help identify areas of potential losses of P.

This study was initiated to investigate the accumulation of P in the soil profile during application of dairy waste effluent to two cropping sequences at two N rates in a deep sandy soil.

Materials and Methods

Experiment Location and Design

The study was located at the North Florida Holstein Dairy facility, which is two miles south of Bell, Florida. A randomized block design containing three blocks and arranged as a split plot was used as the experimental design. Main plots were N loading rates and subplots were cropping systems. Subplot area was 232 m². Dairy waste effluent was used as the N source. The N application rates were 448 and 896 kg/ha/yr which correspond to P loadings of 112 and 224 kg/ha. The cropping systems were corn- forage sorghum-rye and perennial peanut-rye.

Soil Selection and Sampling

The soil was mapped as a Kershaw sand (sandy, thermic, uncoated Typic Quartzipsamments). Soil profile samples (0-15, 15-30, 30-45, 45-60, 60-80, 80-100 cm) were collected from each treatment in 1996 (prior to effluent application) and in 1997 and 1998 (after effluent application). Soil from three profiles in each subplot was collected, composited, mixed thoroughly and a 1-kg subsample was brought to the laboratory for analysis. Soil samples were air-dried and sieved (2mm) prior to analysis. Soil samples were also collected in a similar manner from an adjacent native area believed to be unimpacted by manure or fertilization application.

Soil Characterization

Texture was determined using the pipette method (Day, 1965). Total phosphorus (TP) was determined by ashing 1.0 g of soil for 3 hours and then solubilizing with 6 M HCl (Anderson, 1976). Double-acid (Mehlich I)-extractable P, Al, Fe, Ca and Mg were obtained with a 1:4 soil/double acid ratio (Mehlich, 1953). Phosphorus (P) in solution was analyzed by the molybdenum-blue method (Murphy and Riley, 1962). Soil pH was

determined on 1:2 soil/water ratio, and the organic carbon content of the air-dried samples was determined by combustion (Broadbent, 1965).

Effluent Application and Characterization

Effluent was taken directly from the dairy waste pond on the farm in which the manure flushed from the milking parlor and feed barn is collected. The effluent was applied to the experimental area through a center pivot irrigation system. The annual application of effluent ranged between 355 to 500 mm depending on N application rate and the concentration of N in the effluent. The average annual concentration of TP ranged from 56 mg/L in 1996 to 49 mg/L in 1998, and the soluble reactive phosphorus (SRP) from 44 in 1996 to 47 mg/L in 1998 (Table 2-1).

Table 2-1. Average annual concentrations (mg/L) of ammonium nitrogen ($\text{NH}_4\text{-N}$), total Kjeldahl nitrogen (TKN), soluble reactive P (SRP), and total P (TP) in effluent applied to the study site. Numbers in parentheses are standard deviations.

YEAR	$\text{NH}_4\text{-N}$	TKN	SRP	TP
	mg/L			
1996	172(48)	258(84)	44(14)	56(20)
1997	176(40)	302(75)	44(12)	55(18)
1998	192(51)	280(69)	47(6)	49(20)

Statistical Analysis

Data analyses were done using SAS program (SAS Institute Inc. 1985) (PROC MIXED) procedure (SAS Institute Inc. 1992). The PROC MIXED procedure was selected based on the fact that it is designed for a mixed effect model where random

terms are incorporated into inference from the outset. Contrast, least square means and estimates of linear combinations are reported with correct standard errors. The GLM (General linear Model) which is designed for a fixed effect model, with allowance for certain adjustments in the presence of random terms, needs special attention to be given to least square means and contrast since their standard errors are not necessarily correct. This is true, for example, for split-plot design as is the case for the experimental design in this study (Schabenberger, 1996).

The main difference between PROC MIXED and PROC GLM is that PROC MIXED estimation of variance is based on maximum likelihood while PROC GLM is based on method of moments estimation (ANOVA method) of solving expected mean squares for the variance components (Schabenberger, 1996). Another advantage of PROC MIXED is that it allows data that are missing at random while PROC GLM requires balanced data, and ignore subjects with missing data (Wolfinger and Chang, 1996). This criteria for PROC MIXED was of interest in handling the analysis of this study. This study is a component of a larger project, which include three main treatments (effluent application rate) and five cropping systems as a sub treatments in a split plot design with the aim of comparing their effectiveness in nutrient recovery and maintenance of acceptable levels of N and P in ground water. However, for the purpose of this study, two effluent application rate and two cropping systems were selected under the original experimental design. The selection of PROC MIXED to analyze data of the study offered a means of dealing with unbalanced data. The model used in the analysis included: date, block, rate, crop, and depth and their interactions such as date*rate, date*crop, crop*rate,

date*depth, rate*depth, crop*depth, date*crop*rate, date*rate*depth, date*crop*depth, crop*rate*depth, and date*crop*rate*depth.

Results and Discussion

The study site soil was mapped as Kershaw sand (sandy, thermic, uncoated Typic Quartzipsamments) in the Gilchrist County soil survey report (Soil Survey Staff, Gilchrist County, Florida, 1973). Since the publication of the report, the criterion for coated vs. uncoated family placement has been changed for the USDA soil taxonomic system (Soil Survey Staff, 1999). The sandy materials sampled in this study would meet the criterion for coated (5 percent silt plus 2 times the clay content), based on the particle size analysis (Table 2-2). Also, some auger borings to 2 m revealed spodic horizons which indicated inclusions of Spodosols, and dark colors in the surface horizon in some areas qualify it to be an Umberic epipedon, which would result in classification as an Inceptisol (Umbrept) rather than a Psamment. Nevertheless, the soil was consistently sandy and similar to Kershaw sand with respect to use and management.

Soil Properties Prior to Effluent Application

The soil from the study site prior to effluent application had a different chemical composition than a soil samples from a native site (Table 2-3). Double acid (Mehlich I)-extractable elements and TP concentrations for the study site prior to the application of effluent were higher than the concentrations in soil from the native site (Table 2-3). For example, Mehlich I-extractable Ca for the study site ranged from 968 mg/kg at the surface horizon to 75 mg/kg at the lower depth of the profile (100 cm). Comparable values for the native site were 12 and 4 mg/kg, respectively (Table 2-3). Differences in Ca and Mg content between the native site and the study site prior to the application of

Table 2-2. Selected characteristics of typical Kershaw sand (Soil Survey Staff, Gilchrist County, Florida, 1973) compared to the study site.

Location	Horizon	Depth cm	pH	Org. C	SAND SILT CLAY		
					%		
<u>Native</u>	A	0-18	4.8	0.99	96.5	1.1	2.4
	C1	18-76	5.0	0.39	96.1	1.8	2.1
	C2	76-147	4.9	0.16	97.3	0.4	2.3
	C3	147-203	5.0	0.10	96.1	2.0	1.9
<u>Study Site</u>	A1	0-15	6.2	1.54	93.1	4.8	2.0
	A2	15-30	6.0	0.79	94.1	4.2	1.7
	C1	30-45	6.5	0.71	95.3	3.1	1.6
	C1	45-60	6.5	1.58	95.0	3.8	1.2
	C2	60-80	6.6	0.54	95.4	2.7	1.9
	C2	80-100	6.5	0.43	95.9	2.4	1.7

Table 2-3. Mehlich I-extractable elements concentrations and total P (TP) in "native" soil (n = 3 profiles) and study site (n = 12 profiles) soil profiles prior to beginning of the study.

Location	Depth cm	Ca	Mg	Al	Fe	P	TP
(mg/ kg)							
<u>Native</u>	0-15	11.7	1.9	267	18.4	47	214
	15-30	5.1	1.1	317	20.7	52	270
	30-45	6.0	0.8	330	19.1	39	241
	45-60	4.7	0.7	337	16.3	36	184
	60-80	4.7	0.8	308	16.3	39	181
	80-100	4.1	0.7	280	14.3	33	173
<u>Study Site</u>	0-15	968	115	301	23.5	283	328
	15-30	522	69.3	280	22.8	184	254
	30-45	208	34.1	203	19.6	75	154
	45-60	135	25.7	161	17.9	37	254
	60-80	103	22.9	133	15.9	20	218
	80-100	75	19.2	117	14.5	12	192

effluent were also reflected in a higher pH in all horizons in the study site. The higher pH and organic C in all horizons of the soil from the study site prior to effluent application could be attributed to a previous manure application. Dairy manure can appreciably elevate not only the P, but also other components in soils (Dantzman et al., 1983; Wang et al., 1995). The elevated level of P (TP and Mehlich I- extractable P) in the soil of the study site indicated a previous manure application (Table 2-3). The site appeared to have been heavily loaded with animal waste prior to the start of this study (47 mg/kg Mehlich I-extractable P in the native area vs 283 mg/kg Mehlich I-extractable P in study site surface horizon soils). Several studies (Sims, 1992; Snyder et al., 1993; Sharpley et al., 1994b; Kingery et al., 1994; Graetz & Nair, 1995; Wang et al., 1995) have shown that manure application usually results in an increase in TP, STP and other components in soil.

Effect of Application Rate and Cropping Systems

Statistical evaluation of TP data (Table 2-4) shows that date and depth were significant at the 0.0001 probability level, but date*depth and date*crop was also significant at 0.0001. However, neither the single effect of crop (cropping system), nor the rate (effluent application rate) was significant. Therefore, a higher level of significance such as date*depth and date*crop will be reported and interpreted, when it was appropriate. Means comparison was done when there was a significant interaction by SAS code (pdiff) for differences between least squares means (LSM).

Total P (TP) increased over time (1996 vs. 1998). The effect of date*depth was significant ($P < 0.01$) to the depth of 45 cm which reflects a buildup of total P in the soil profile. Also, the effect of date*crop was significant ($P < 0.01$) which might imply a role

Table 2-4. Statistical evaluation of TP data for the three-year study period.

Source	NDF	DDF	Type III F	Pr > F
Date	2	96	36.31	0.0001
Block	2	2	0.46	0.6867
Rate	1	2	0.37	0.6063
Date*Rate	2	96	2.65	0.0760
Crop	1	44	0.15	0.7001
Date*Crop	2	96	7.47	0.0010
Crop*Rate	1	44	1.18	0.237
Date*Crop*Rate	2	96	0.83	0.4412
Depth	5	44	46.25	0.0001
Date*Depth	10	96	15.82	0.0001
Rate*Depth	5	44	1.21	0.3226
Date*Rate*Depth	10	96	1.14	0.3395
Crop*Depth	5	44	0.84	0.5263
Date*Crop*Depth	10	96	1.69	0.0937
Crop*Rate*Depth	5	44	0.6	0.6410
Date*Crop*Rate*Depth	10	96	1.08	0.3853

for the cropping system on P removal. The application of effluent at both rates (448 and 896 kg N/ha per year) increased TP content of the soil and the increase was dependent on the effluent application rate. Total P in the surface horizon increased from 312 to 753 mg/kg at the end of the study under the high application rate (Fig. 2-1) and from 343 to 485 mg/kg under the low application rate (Fig. 2-2). A higher TP content in soil impacted by dairy waste application is common. Graetz and Nair (1995) reported up to 1885 mg/kg of TP in the soil surface horizon of dairy intensive areas.

The application of effluent also had an effect on Mehlich I-extractable P. The effect of date*depth ($P<0.05$) and rate*crop ($P<0.01$) on Mehlich I-extractable P were significant. During the two year of effluent application, Mehlich I-extractable P decreased in the surface horizon but increased in the lower horizons (Fig. 2-3). The decrease of Mehlich I-extractable P in the surface horizon and the increase in the lower depths of the profile may be attributed to both crop uptake of P and the leaching effect of effluent irrigation. Mozaffari and Sims (1994) measured soil test P (Mehlich I) values with depth in cultivated and wooded soils on farms impacted by poultry litter applications, and observed leaching to depth of ~ 60 to 75 cm. Soil test P values were very high in topsoils relative to those considered optimum for most crops. Also, King et al. (1990) examined the effect of 11 years of swine lagoon application on P distribution and reported soil test P (Mehlich I) values much greater than required for crop production (225-450) mg/kg. Soil test P at the 15-30, 30-45, 45-60, and 60-75 cm depth was 120, 75, 25, and 5 mg/kg at the lowest effluent rate (335 kg N/ha per year) and 350, 175, 125, and 50 mg/kg at the highest effluent rate (1340 kg N/ha per year). Soil test P (Mehlich I) values for soil samples from the study site at 15-30, 30-45, 45-60, and 60-80 cm depth

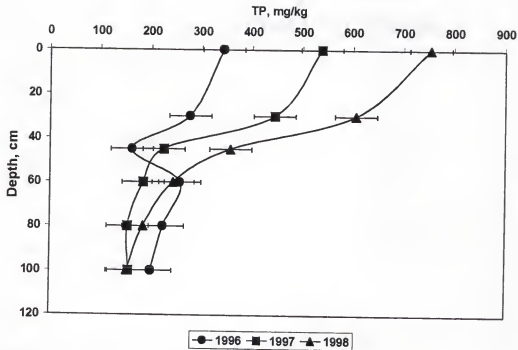


Figure 2-1. Average total P (TP) concentrations in the soil profile under the high rate application prior to application of effluent (1996) and after effluent application (1997 and 1998). Values are LSM \pm Std. Error.

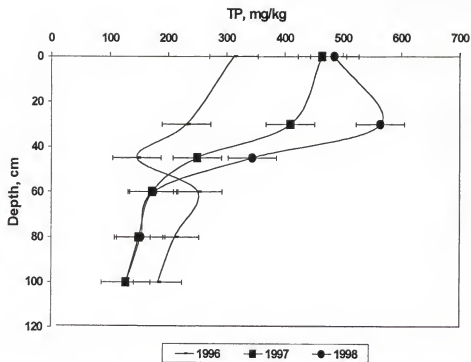


Figure 2-2. Average total P (TP) concentrations in the soil profile under the low rate application prior to application of effluent (1996) and after effluent application (1997 and 1998). Values are $LSM \pm Std. Error$.

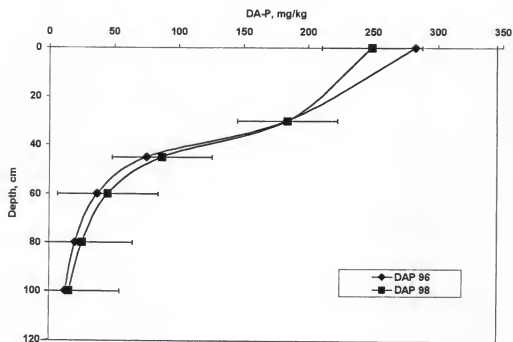


Figure 2-3. Mehlich I-extractable P concentrations in the soil profile prior to start of the study and after two years of effluent application (1998). Values are $LSM \pm Std. Error$.

were 197, 93, 55, and 32 mg/kg at the highest rate (896 kg N/ha per year) and 157, 62, 41 and 22 at the lowest rate (448 kg N/ha per year). These values of soil test P for the soil samples from the study site after two year of effluent application should be looked at in the context of high Mehlich I extractable P existing prior to the start of the study (Table 2-3). However, as for the rate*crop effect, Mehlich I-extractable P concentration was higher for P-R (perennial peanut-rye) than for C-FS-R (corn-forage sorghum-rye) cropping system under the high rate application (Fig. 2-4). This finding suggests that the C-FS-R (corn-forage sorghum-rye) cropping system may be more effective in P removal than the P-R cropping system. Only a slight change in Mehlich I-extractable P between the two cropping systems was observed under the low application rate (Fig. 2-5). In spite of the suggested higher P removal by the C-FS-R cropping system than the P-R cropping system, the level of double acid (Mehlich I)-extractable P concentration in the study prior to effluent application is considered to be extremely high relative to the optimum for crop production when compared to levels reported by other studies (Kingery et al., 1994; Mozaffari and Sims, 1994) and the removal by the cropping systems did not alter the high level of STP. Such high level of STP can lead to leaching to a deeper depth in the soil profile.

Although double acid may not extract the total amounts of reactive elements for P retention, double-acid (Mehlich I)- extractable P was highly correlated with Ca, Mg, Al, and Fe extracted by Mehlich I solution, with 93% of variability explained by this relationship (Table 2-5).

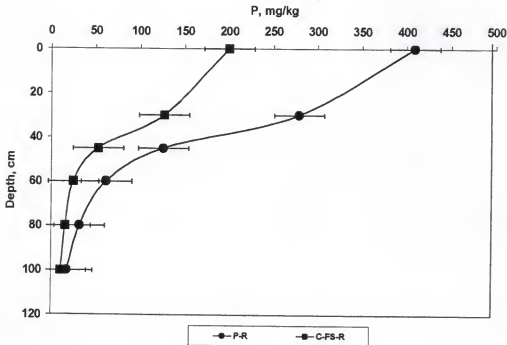


Figure 2-4. Mehlich I-extractable P concentrations for cropping systems under the high rate effluent application in 1998. Values are LSM \pm Std. Error.

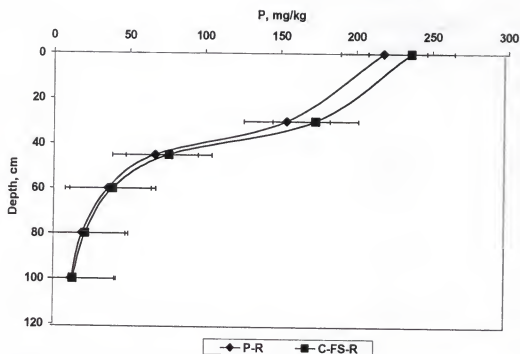


Figure 2-5. Mehlich I-extractable P concentrations for cropping systems under the low rate effluent application in 1998. Values are LSM \pm Std. Error.

Table 2-5. Regression equation relating Mehlich I-P to the independent variables Mehlich I-Ca, Mg, and Fe. (n=432).

Equation	Model R ²
$M I-P = -56.9 + 0.272 M I-Ca^{***} - 0.284 M I-Mg^{*} + 0.233 M I-Al^{***} + 1.55 M I-Fe^{***}$	0.932***

***, *, Significant at $p < 0.001$, and $p < 0.05$ respectively. N.S. Not significant.

Summary and Conclusions

The soil at the study site has been mapped as Kershaw sand and is considered uncoated. However, some coatings are evident based on the color of the sand grain and the USDA taxonomic criterion of >5% silt plus (2 times the clay content) for coated family placement (Soil Survey Staff, 1999). Sands that retain coating components should have a higher affinity to retain P than do bare quartz grains (Harris et al., 1996), a criterion that is favorable for this study. The soil at the study site appeared to have been heavily loaded with animal waste prior to the start of this study. Mehlich I-extractable P in the surface horizon of the native area was 47 mg/kg vs. 283 mg/kg Mehlich I-extractable P in the study site surface horizon soils. Mehlich I-extractable P levels in topsoils at the study site was high relative to those considered optimum for agronomic crops and raise the question about the suitability of the effluent application rates used. The effluent application rates selected were based mainly on estimated N removal for the forage crops within the cropping systems and experimental purposes outlined in the main project objectives.

The previous application of dairy manure to the study site prior to the start of the study resulted also in a higher Ca^{+2} and Mg^{+2} content throughout the soil profile

compared to the native site, although the amount and date could not be established. The application of dairy waste effluent at both rates (448 and 896 kg N/ha per year) over a 2-year period increased the TP content in the soil profile to the 45 cm depth. The increase in TP was significant and dependent on the effluent application rate. The application of effluent also had an effect on the Mehlich I-extractable P. The effect of date*depth and rate*crop on Mehlich I-extractable P were significant. During the two year of effluent application Mehlich I-extractable P decreased in the surface horizon but increased in the lower horizons. The decrease of Mehlich I-extractable P in the surface horizon and the increase in the lower depths of the profile may be attributed to both crop uptake of P and the leaching effect of effluent irrigation. However, as for the rate*crop effect, Mehlich I-extractable P concentrations were higher for P-R (perennial peanut-rye) than for C-FS-R (corn-forage sorghum-rye) cropping system under the high rate application. This finding suggests that the C-FS-R (corn-forage sorghum-rye) cropping system may be more effective in P removal than the P-R cropping system. Only a slight change in Mehlich I-extractable P between the two cropping systems was observed under the low application rate. However, the removal by the cropping systems did not alter the high level of STP that already existed. Thus, to prevent an accumulation of excessive P content in the soil profile, history of the land, application rate, and cropping systems estimated removal of P should be considered.

CHAPTER 3

PHOSPHORUS FORMS AND FRACTIONATION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT

Introduction

Sequential extraction schemes using various chemical extracts have been developed through the years to quantify and fractionate the different forms of P in soils. The objectives of P fractionation in general are to provide insight into the fate and transformation of P added to soils as fertilizers or manure, estimate the availability of P to plants for agronomic purposes, estimate the potential for P movement from erosion and through leaching, and provide information regarding the interaction between P in sediments and the overlaying water in the case of aquatic systems (Graetz and Nair, 1999). The underlying assumption here is that inorganic P in soil consists of varying proportion of three discrete classes of compounds, namely, Fe, Al and Ca phosphate, some of which could be occluded or enclosed within coating of Fe oxides and hydrated oxides. These chemical P forms are operationally defined on the basis of reactivity of a particular phase in a given extractant and subject to several interpretations. Nevertheless, they offer a convenient means for obtaining significant information on P chemistry of soils (Nair et al., 1995). Fractionation of P forms has been particularly useful in understanding the transformation of P added to soil, either in inorganic or organic amendments such as manures. Zhang and Mackenzie (1997) used P fractionation and path analysis to compare the behavior of fertilizer and manure-P in soils. Their results showed that P behaves differently when added as manure, compared to inorganic

fertilizer, which may affect the depth of P movement through the soil profile. Simard et al. (1995) reported that a significant portion of the P moving downward in soils receiving substantial amounts of animal manure accumulated in labile forms such as water-soluble, Mehlich-3, and NaHCO_3 extractable P forms. Eghball et al. (1996) found that P from manure moved deeper in the soil than P from chemical fertilizer in long term (>50 yr) studies. Nair et al. (1995) studied the forms of P in soil profiles from dairies of south Florida and illustrated the fate and transport of P in these systems. They identified the P forms in the soil profile of differentially manure-impacted soils in the Okeechobee watershed, Florida. All soils were Spodosols, and soils were collected by horizon, A, E, Bh, and Bw. Their results showed no statistical differences in the percentage of labile P (NH_4Cl -extractable P), the P that would most likely move from the A horizon of the various components. The labile P form for the A horizon of all dairy components averaged 9%. However, more P will be lost from the heavily manure-impacted intensive areas with high total P values, than from the less impacted pasture, forage and native areas. They also observed that the P would continue to be lost from dairies that have been abandoned for a considerable period of time. The P that leaves the surface horizon might be lost through surface and subsurface drainage, and the portion that reaches the spodic (Bh) horizon will be held as Al- and Fe-associated P, either in the inorganic or in the organic fraction. The high percentage of HCl-extractable P (Ca- and Mg-associated P) in the A horizon of the intensive dairy component was also of potential concern. Such P could be continuously extracted by NH_4Cl or by water, suggesting that about 80% of the total soil P had the potential to move eventually with drainage water into Lake Okeechobee (Graetz and Nair, 1995).

Recently, other watersheds in Florida such as the Middle Suwannee River area have become the focus of attention. Soils in this area include Entisols; soils lacking diagnostic horizons and other features that are specifically defined and required for other orders of the USDA taxonomic system (Soil Survey Staff, 1994). Quartzipsamments, the only Psamment Great Group which occurs in Florida, are in central northern peninsular Florida and most prevalent on well to excessively drained landscapes (Harris and Hurt, 1999). The sandy nature of Quartzipsamments result in relatively low P retention or capacity. Therefore, an understanding of P forms in such soil receiving dairy manure effluent application could help identify areas of potential losses of P.

Materials and Methods

Experiment Location and Design

The study site was located at North Florida Holstein Dairy facility, which is two miles south of Bell, Florida. A randomized block design containing three blocks and arranged as a split plot was used as the experimental design. Main plots were N and P loading rates and subplots were cropping systems. Subplot area was 232 m². Dairy waste effluent was used as the N source. The N application rates were 448 and 896 kg/ha/yr, which correspond to P loading of 112 and 224 kg/ha/yr. The cropping systems were corn-forage sorghum-rye and perennial peanut-rye.

Soil Selection and Sampling

The soil was mapped as Kershaw (sandy, thermic, uncoated Typic Quartzipsamments). Soil profile samples (0-15, 15-30, 30-45, 45-60, 60-80, 80-100 cm) were collected in 1996 (prior to effluent application) and in 1997 and 1998 (after effluent application). Soil from three profiles in each subplot was collected, composited, mixed

thoroughly and a 1-kg subsample was brought to the laboratory for analysis. Soil samples were air-dried and sieved (2mm) prior to analysis. In addition to soil samples from the study site, soil samples were also collected in a similar manner from an adjacent native area believed to be unimpacted by manure or fertilization application.

Fractionation Scheme

The scheme used to fractionate soil-P was a modification of that of Hieltjes and Lijklema (1980) by Nair et al., (1995). A 1-g air dried sample was sequentially extracted twice with 25 mL of 1 M NH_4Cl (adjusted to pH 7.0) with two hours shaking, 0.1 M NaOH with seventeen hours shaking, and 0.5 M HCl with 24 hours shaking. The 1: 25 soil: solution ratio was selected based on preliminary investigations as shown in APPENDIX. After each extraction, the content were centrifuged for 15 min at 3620 x g and filtered through a 0.45- μm filter. All extractions were carried out at room temperature. Residual P was determined by ashing previously extracted soil sample for three hours and then solubilizing with 6 M HCl (Anderson, 1976). A 5 mL of the NaOH extract was also digested by persulfate-sulfuric acid mixture at 380°C (APHA, 1985) to determine moderately labile organic P as the difference between P in digested and undigested NaOH extract. NH_4Cl -extractable P was defined as labile P (Pettersson and Istvanovics, 1988), NaOH-extractable P as Fe-Al-associated P, and HCl-extractable P as Ca-Mg-associated P. Residual P is the P that is not readily removed by any of the above chemical extractants. Total phosphorus (TP) was determined by ashing 1.0 g of soil for 3 hours and then solubilizing with 6 M HCl (Anderson, 1976). Double-acid (Mehlich I)-extractable P, Al, Fe, Ca and Mg were obtained with a 1:4 soil/double acid ratio (Mehlich, 1953). Phosphorus (P) in solution was analyzed by the molybdenum-blue

method (Murphy and Riley, 1962) on a spectrophotometer at wavelength of 880 nm.. Soil pH was determined on 1:2 soil/water ratio, and the organic carbon content of the air-dried samples was determined by combustion procedure (Broadbent, 1965). Texture was determined using the pipette method (Day, 1965).

Statistical Analysis

Data analyses were done using SAS program (SAS Institute Inc. 1985) (PROC MIXED) procedure (SAS Institute Inc. 1992). Relationships among parameters were evaluated using linear correlation. Multiple regression was used to examine the strength of the relationships between parameters.

Results and Discussion

Inorganic Fe/Al associated P constituted the major proportion of TP in the soil profile of the study site prior to effluent application. As concluded from Chapter 2, the soil at the study site appeared to have been heavily loaded with animal waste prior to the start of this study, although amount and dates could not be established. Phosphorus originally present in the soil profile in 1996 (prior to effluent application) was largely in the form of inorganic Fe/Al-associated P, which ranged from 292 mg/kg in the surface horizon to 76 mg/kg in lower depth (100 cm) (Table 3-1). These values of Fe/Al- P corresponded to 62% and 49% of TP, respectively (Table 3-2). The application of effluent increased this fraction to 362 mg/kg in the surface horizon in 1998 with smaller increase throughout the soil profile (Fig. 3-1). A comparison of Fe/Al-P mean concentration in each depth within the soil profile at the beginning (1996) and end of the study period (1998) showed that the increase was statistically significant ($P < 0.001$ - $P < 0.05$) at the surface and down to the 45 cm depth (Table 3-3). The predominance of

Table 3-1. P values (mg/kg) in each fraction within a soil depth increment at the beginning (1996) and end of the study period (1998) (n = 12 profiles). Values are Least Square Means (LSM).

Depth (cm)	Labile	Al-Fe	Ca-Mg mg/kg	Residual
	1996			
0-15	85	292	50	36
15-30	61	221	30	22
30-45	36	146	21	16
45-60	44	106	12	25
60-80	37	87	09	29
80-100	37	76	12	25
	1998			
0-15	97	362	52	59
15-30	93	317	30	40
30-45	80	205	17	28
45-60	77	137	13	23
60-80	71	101	07	23
80-100	69	81	07	19

Table 3-2. Percentage of P in each fraction within a soil depth increment at the beginning (1996) and end of the study period (1998)(n = 12 profiles). Values are Least Square Means (LSM).

Depth (cm)	Labile-P	Al-Fe-P	Ca-Mg-P %	Residual-P	Sum of P fraction mg/kg
1996					
0-15	18.3	62.6	10.8	8.30	463
15-30	18.4	65.3	9.20	7.10	334
30-45	16.8	64.5	10.5	8.20	219
45-60	24.8	54.9	7.00	13.3	187
60-80	24.3	52.3	5.80	17.0	162
80-100	26.3	49.4	8.20	16.1	150
1998					
0-15	17.0	63.5	9.1	10.3	570
15-30	19.4	66.0	6.2	8.30	480
30-45	24.2	62.1	5.1	8.50	330
45-60	30.8	54.8	5.2	9.20	250
60-80	35.1	50.0	3.5	11.4	202
80-100	39.2	46.0	4.0	10.8	176

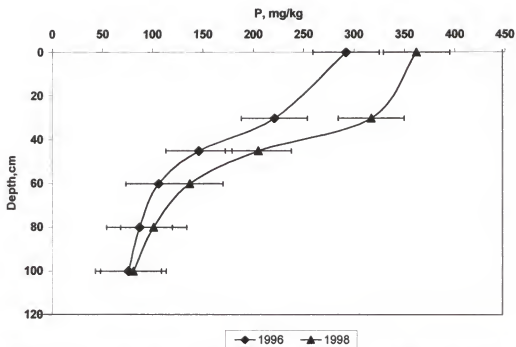


Figure 3-1. Al-Fe-associated P (mg/kg) within the soil profile at the beginning 1996 and end of the study period (1998). Values are LSM \pm Std. Error.

Table 3-3. Increases in each fraction within a soil depth increment between the beginning (1996) and end of the study period (1998).

Depth (cm)	Labile mg/kg	Al-Fe mg/kg	Ca-Mg mg/kg	Residual mg/kg
0-15	11.75*	69.76**	NS	22.31**
15-30	31.62**	95.69**	NS	17.69**
30-45	44.55**	59.03**	NS	23.9**
45-60	33.38**	31.0*	NS	NS
60-80	34.52**	NS	NS	NS
80-100	31.44**	NS	NS	NS

*, ** Significant at the .05 and .001 probability levels, respectively; NS = none significant.

Fe/Al-associated P in surface horizon and throughout the profile was a reflection of the properties of soil and the dairy waste effluent used. The soil at the study site, as mentioned in Chapter 2, was classified as coated sand with low clay content, low organic matter, pH of 6-6.5, and a higher Mehlich I- extractable P (Table 3-4) in comparison to soil from a native area (283 vs. 47 mg/kg). The soil from the native area, which has a low content of clay, organic matter, moderately low pH (4-4.5), and a high Mehlich I- extractable Al/Fe, compared to the rest of cations in the soil, was a typical example of predominance of P retention by Al/Fe oxides. Further more, P fractionation of soil samples from the native area showed that up to 62% of TP was in the form of Al/Fe-associated P (Tables 3-5 and 3-6).

The predominance of Al/Fe-associated P in the soil samples from the study site was a reflection of its original properties, and its increase after effluent application could be a consequence of adsorption under continuous application of a soluble P. The dairy waste effluent contained 55 mg P/kg, 78% of which was soluble reactive P (SRP). The difference between pH values of soil sample from the study site and native area, and the presence of a higher Mehlich I-extractable Ca content in soil samples from the study area did not seem to alter the predominance of Al/Fe-associated P in the P fractionation scheme.

Labile-P or easily removable P as defined by (Pettersson and Istvanovics, 1988) constituted 18-40% of TP in the soil profile of the study site. Prior to effluent application in 1996, labile-P ranged from 85 mg/kg in the surface horizon to 37 mg/kg in the lower depth (100 cm) (Table 3-1) which corresponds to 26 and 18% of TP, respectively (Table 3-2). The application of effluent increased this fraction to 97 mg/kg in surface horizon

Table 3-4. Mean concentration of Mehlich I extractable elements (mg/kg) in the soil profile of the study site in 1996 prior to the application of effluent (n = 12 profiles).

Location	Depth (cm)	Mehlich I Extractable Elements (mg/kg)			
		Ca	Mg	Al	Fe
<u>Study Site</u>	0-15	968	115	301	23
	15-30	522	69	280	23
	30-45	208	34	203	20
	45-60	135	26	161	18
	60-80	103	23	133	16
	80-100	75	19	117	14

Table 3-5. P values (mg/kg) in each of the fractions within a soil depth increment at the native site (n = 3 profiles). Values are Least Square Means (LSM).

Depth (cm)	Labile P	Al-Fe P mg/kg	Residual P	Ca-Mg P	Sum of P Fractions mg/kg
0-15	68	125	3	6	202
15-30	59	195	20	12	26
30-45	58	166	4	13	241
45-60	58	136	17	8	219
60-80	58	150	17	9	234
80-100	61	149	16	9	235

Table 3-6. Percentage of P in each of the fractions within a soil depth increment at the native site (n = 3 profiles). Values are Least Square Means (LSM).

Depth (cm)	Labile P	Al-Fe P %	Ca-Mg P	Residual P
0-15	33	62	3	2
15-30	20	68	4	7
30-45	23	69	5	2
45-60	26	62	4	8
60-0	24	64	4	7
80-100	26	63	4	7

and 69 mg/kg in the lower depth (100 cm) (Table 3-1) and (Fig. 3-2). Labile-P (Fig. 3-2) increased in the surface horizon and throughout the profile over time (1996 vs. 1998) with a substantial increase in the lower depth accounting for 40% of TP in 1998 (Table 3-2). A comparison of labile-P mean concentration in each depth within the soil profile at the beginning (1996) and end of the study period (1998) showed that the increase was statistically significant ($P < 0.001$ - $P < 0.05$) at the surface and throughout the profile (Table 3-3). The previous mentioned studies by Nair et al. (1995) and Graetz and Nair (1995) has reported that labile P form for the A horizon of Spodosol in all dairy components averaged 9% in a single NH_4Cl extraction and 1: 10 soil: solution ratio. The higher percentage of labile P form in this study throughout the profile and its substantial increase in the lower depth after effluent application is likely due to rapid movement of P through the profile.

In this study, the Ca and Mg-associated P fraction was the only fraction that remained constant and did not show change with the application of effluent over time (Table 3-1 and 3-2); (Fig. 3-3) in spite of considerable Mehlich I extractable-Ca content throughout the soil profile as shown in Table 3-4. Though the stability of P forms is not addressed in this study, Harris et al. (1994) reported an absence of Ca-P minerals despite high pH and years of high Ca and P additions in soils from intensive areas of dairies in south Florida. The lack of crystalline Ca-P could be related to kinetics, or to a poisoning effect of component such as Mg, Si and organic acids in the dairy soil system (Wang et al., 1995). The absence of a significant change in the Ca/Mg-associated P pool, in this study, could be due to the factors mentioned by Wang et al., 1995 or due to analytical

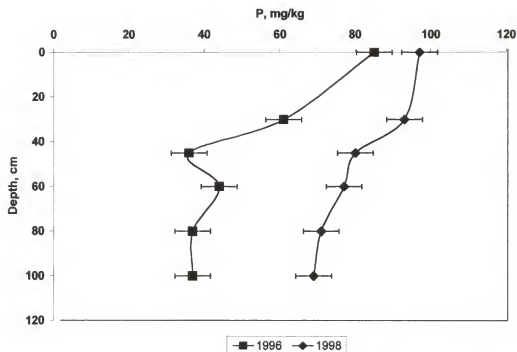


Figure 3-2. Labile P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are LSM \pm Std. Error.

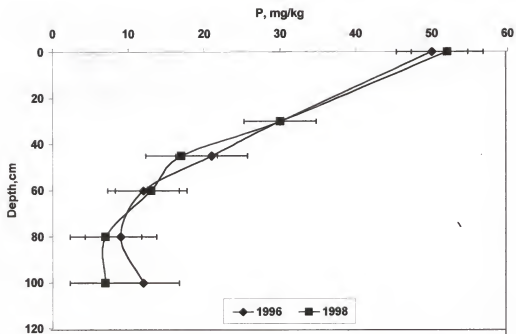


Figure 3-3. Ca-Mg associated P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are LSM \pm Std. Error.

limitation. Nair et al. (1995) noticed that the labile P fraction increased if the soil was repeatedly extracted with the 1 M NH_4Cl solution, with a corresponding decrease being noted for the HCl P fraction (Ca/Mg-associated P pool).

Residual-P, the P fraction that is not readily removed by any of the chemical extractants, constituted 7 to 17% of TP in the soil profile of the study site in 1996 prior to the application of effluent (Table 3-1). This percentage corresponded to 25 and 36 mg P/kg, respectively (Table 3-2). The application of effluent increased this fraction to 59 mg P/kg at the surface horizon in 1998 (Table 3-1) and (Fig. 3-4). However, as a percentage of TP this amount constituted 10% of total P (Table 3-2). Bowman et al., 1998 used both terms resistant P and residual P to mean that pool which is extracted with great difficulty, or by difference from the whole when a soil residue yields essentially no more acid- and base-extractable inorganic P (P_i) and organic P [P_o , as determined by difference ($\text{P}_t - \text{P}_i$)]. They reported an average of about 26% of TP as resistant, with the more weathered soil containing about 50% resistant P. Nair et al. (1995) studied the distribution of P forms of two abandoned dairies (12 and 18 yr) compared with the youngest active (8 yr) dairy and reported an increase in Ca/Mg-associated P (61-74 %) and a decrease in residual P (20 to 11%) in the A horizon of the abandoned dairies in south Florida. They related this trend to a possible gradual mineralization of the residual P, if the residual P is primarily recalcitrant organic P. However, the trend of increasing residual P content in this study could be related to certain components in the effluent used. The fractionation scheme used in this study did not offer a way of fractionating residual P into organic and inorganic forms.

The trend of distribution of different P pools in this two year study was

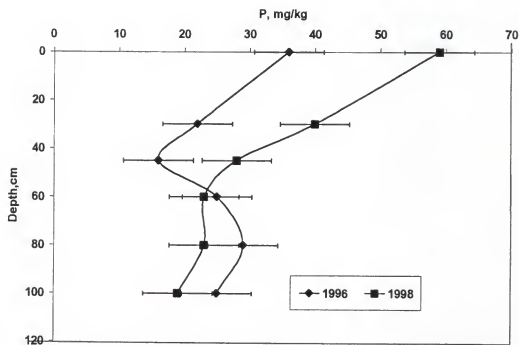


Figure 3-4. Residual-P values (mg/kg) within the soil profile at the beginning (1996) and end of the study period (1998). Values are $\text{LSM} \pm \text{Std. Error}$.

that Al-Fe- associated P constituted the major proportion of TP in soil profile followed by labile-P (prior to effluent application) and that both showed an increase with the application of effluent. The increase of labile-P in the lower depth of the soil profile after effluent application could be an indication of downward P movement in the soil profile.

Previous research in forms of P in soil profile from dairies of south Florida by Graetz and Nair (1995) reported a predominance of Al/Fe-P (49% of TP) in the A horizon of Spodosol soils from nonimpacted areas. However, the predominant form of P in the A horizon of highly manure-impacted areas (active dairies for up to 32 years) was Ca/Mg-P which reflect the predominance of Ca/Mg in cattle manure in their case. They also reported that high percentage of HCl-extractable P (Ca/Mg-associated P) in the A horizon of the intensive dairy component was of potential concern. This P could be continuously extracted by NH_4Cl or by water, suggesting that about 80% of the total soil P had the potential to move eventually with drainage water into Lake Okeechobee (Nair et al., 1995).

Summary and Conclusions

Most of P in the soil profile of the study site (prior to effluent application) consisted of Fe/Al-associated P, which accounted for 49-62% of TP. The application of effluent resulted in an increase in this fraction throughout the soil profile. Labile-P constituted 18-26% of TP in the soil profile of the study site prior to effluent application, and the application of effluent increased this fraction significantly up to 40% of TP at the lower depth of the profile (100-cm). The increase in labile-P at the lower depth (100-cm) of the soil profile after two years of effluent application could be an indication of downward P movement in the soil profile. Ca/Mg-associated P was the only fraction that

remained constant and did not show change with the application of effluent over time. However, the absence of a significant change in Ca/Mg-associated P in this study could be due to analytical limitation. Nair et al. (1995) noticed that the labile P fraction increased if the soil was repeatedly extracted with the 1 *M* NH₄Cl solution, with a corresponding decrease being noted for the HCl- P fraction (Ca/Mg-associated P pool).

CHAPTER 4 PHOSPHORUS RETENTION IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT

Introduction

Sandy soils generally retain less P than finer textured soils because of a deficiency of mineral components having surface affinity for orthophosphate. Thus, subsurface transport of P can be significant in sandy soils due to low surface area or a paucity of P-retaining components (Reddy et al., 1996). However, sand-grain coatings could significantly enhance P adsorption and resistance to desorption (Harris et al., 1996). Phosphorus retention in such soil has been the focus of a number of studies due to its relevant environmental consideration in areas of intensified animal-based agriculture (Mozaffari and Sims, 1993; Harris et al., 1994; Graetz and Nair, 1995; Nair et al., 1998; Nair et al., 1999). Furthermore, attempts have been made to use a single-point isotherm to characterize P retention in such soils (Mozaffari and Sims, 1993; Harris et al., 1996; Nair et al., 1998). A single point isotherm indexing approach, termed the relative phosphorus adsorption (RPA) index, effectively arrayed sandy Florida soil samples with respect to relative P adsorption (Harris et al., 1996).

Although the equilibrium P concentration in the soil solution is generally relatively low, recent studies have shown that the P concentration in the soil solution can increase significantly well before the soil adsorption maximum has been reached (Breeuwsma and Silva, 1992). The Dutch have developed a test referred to as the

“Degree of P Saturation” (DPS) which relates the soil P sorption capacity to an extractable P concentration as follows:

$$DPS = \frac{\text{Extractable soil P}}{\text{P sorption maximum}} \times 100$$

Operationally, DPS can be defined as oxalate-extractable P divided by the phosphate sorption capacity of the soil that is estimated from equations including oxalate-extractable Fe and Al (Breeuswma et al., 1995) as follows:

$$DPS = \frac{P_{ox}}{Fe_{ox} + Al_{ox}} \times 100$$

The Dutch used a reference soil solution concentration of 0.1 mg P/L as a critical concentration based on water quality studies. They found that a DPS value of 25% would generally result in soil solution concentration equal to greater than 0.1 mg P/L. Pautler and Sims (1998) study on comparison of short-and long-term sorption kinetics in Atlantic coastal plain soils concluded that the potential for P loss from over-fertilized soils can be improved by a knowledge of DPS of soils.

Sharpley (1995) found a single relationship (r^2 of 0.86) to describe the concentration of dissolved phosphate (DP) as a function of P-sorption saturation for ten soils ranging from sandy loam to clay in texture. The Mehlich-3 extractant was used for extractable soil P and the Langmuir P-sorption maximum as P-sorption capacity in the calculation of DPS.

This study was conducted to evaluate the P retention of a sandy soil under dairy effluent application using traditional multipoint isotherms, RPA, and DPS.

Materials and Methods

Experiment Location and Design

The site of the study was located at North Florida Holstein Dairy facility, which is two miles south of Bell, Florida. A randomized block design containing three blocks and arranged as a split plot was used as the experimental design. Main plots were N loading rates and subplots were cropping systems. Subplot area was 232 m². Dairy waste effluent was used as the N source. The N application rates were 448 and 896 kg/ha/yr which correspond to P loading of 112 and 224 kg/ha/yr. The cropping systems were corn-forage sorghum-rye, and perennial peanut-rye.

Soil Selection and Sampling

The soil was mapped as a Kershaw sand (sandy, thermic, uncoated Typic Quartzipsamments). Soil profile samples (0-15, 15-30, 30-45, 45-60, 60-80, 80-100 cm) were collected in 1996 (prior to effluent application) and in 1997, and 1998 (after effluent application). Soil from three profiles in each subplot was collected, composited, mixed thoroughly and a 1-kg subsample was brought to the laboratory for analysis. Soil samples were air-dried and sieved (2mm) prior to analysis. Soil samples were also collected in a similar manner from an adjacent native area believed to be unimpacted by manure or fertilization application.

Soil Characterization

Rapid chemical assessment of relative phosphorus adsorption (RPA) was done by procedure developed by Harris et al., (1996). Ten- gram samples of air-dry soil were weighed into 20-mL scintillation vial and 2 mL of a 2000 mg/L P solution was added. The content of the vials were mixed by vigorous shaking, and allowed to equilibrate for 24 hours at room temperature. The contents were transferred from the vials to centrifuge

tubes, and centrifuged at 1500 g for 5 min. The centrifuge tubes had small holes drilled through the bottom. During centrifugation, solution passed through the holes into small cups attached to the bottom of the centrifuge tubes. Solution was removed from the cups and passed through a 0.45- μ m syringe filter. Phosphorus in the solution was determined by the method of Murphy and Riley (1962) at an absorbance at 880 nm. The relative P adsorption capacity was quantified by dividing the absolute amount of P adsorbed by the maximum possible under these conditions, which was 400 mg/kg.

Phosphorus multipoint adsorption isotherms were measured using 2 g of an air-dried soil treated with 20 mL of 0.01M KCl solution containing various levels of P (0, 0.2, 0.5, 1, 5, 10, 40, and 100 mg/L) in 50-mL centrifuge tubes. The tubes were placed on a mechanical shaker for 24 hours equilibration period. At the end of 24 hours period, the soil was centrifuged at 3620 x g for 10 min. The supernatant was then filtered through a 0.45- μ m membrane filter and the filtrate analyzed for P (Murphy and Riley, 1962).

Total phosphorus (TP) was determined by ashing 1.0 g of soil for 3 hours and then solubilizing with 6 M HCl (Anderson, 1976). Double-acid (Mehlich I)-extractable P, Al, Fe, Ca and Mg were obtained with a 1:4 soil/double acid ratio (Mehlich, 1953). Phosphorus in solution was analyzed by the molybdenum-blue method (Murphy and Riley, 1962). Soil pH was determined on 1:2 soil/water ratio, and the organic carbon content of the air-dried samples was determined by combustion (Broadbent, 1965). Texture was determined using the pipette method (Day, 1965).

Oxalate-extractable P, Al, and Fe were determined by extraction with an ammonium oxalate (0.1 M oxalic acid + 0.175 M ammonium oxalate) solution adjusted to pH 3.0 (McKeague and Day, 1966). The suspension was equilibrated for 4 hours with

continuous shaking, centrifuged, filtered through a 0.45- μm filter and analyzed for P, Al, and Fe.

Calculations

Degree of P saturation (DPS) was calculated as oxalate-extractable P divided by the P sorption capacity of the soil, which is estimated as the sum of oxalate-extractable Fe and Al (Breeuwsma et al., 1995). This DPS is referred to in this study as (DPS - 1). Also, DPS was calculated as double acid (Mehlich D)-extractable P divided by the P sorption capacity of the soil, estimated from the sum of oxalate-extractable Fe and Al. This DPS is referred to as (DPS - 2).

$$\text{DPS} = \frac{\text{Extractable soil P}}{\text{P-sorption capacity}} \times 100$$

P sorption capacity was estimated from oxalate-extractable Al and Fe.

Adsorption parameters were calculated using the Langmuir adsorption equation:

$$C/S = 1/kS_{\text{max}} + C/S_{\text{max}}$$

Where

$S = S' + S_0$ the total amount of P sorbed, mg/kg

$S' = P$ sorbed by the solid phase, mg/kg

S_0 = originally sorbed on the solid phase, mg/kg

C = concentration of P after 24 h equilibration, mg/L

S_{max} = P sorption maximum, mg/kg

k = constant related to the bonding strength, L/mg P

S_0 was estimated using a least square fit of S' measured at low equilibrium concentration, C . At these concentrations, the linear relationship between S' and C can be

described by $S' = K C - S_0$ where K is the linear adsorption coefficient (Graetz and Nair, 1995). P_0 (soluble P) referred to P in solution after a 24-h equilibrium period when no P was added.

Equilibrium P concentration (EPC), was defined as the concentration of P in solution where adsorption equal desorption and was the value of C when $S' = 0$.

Statistical Analysis

Data analyses were done using SAS (SAS Institute Inc. 1985) program (PROC MIX) procedure (SAS Institute Inc. 1992). Relationships among parameters were evaluated using linear correlation. Multiple regression was used to examine the strength of the relationships between parameters.

Results and Discussion

Relative Phosphorus Adsorption (RPA)

After two years of effluent application, RPA values of soil samples from the study site did not show any significant change and remained in the same range reported before effluent application (Table 4-1). The absence of significant differences in RPA values pre and after effluent application, indicated that effluent application did not influence P sorption capacity for this soil which has been heavily loaded with animal manure prior to the start of the study.

The RPA values of soil samples from the study site ranged from 0.5 to 0.6 throughout the profile pre-and post effluent application (Table 4-1). The samples from native area adjacent to the study site showed an RPA value of 0.8 to 0.9 through out the soil profile (Table 4-1). However, part of this difference could be due to differences in clay content between native and study site samples as shown in Chapter 2 (Table 2-3).

Table 4-1. RPA values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native soil" (n = 1 profile). Values are Least Square Mean (LSM).

Depth	1996	1997	1998	Native
0-15	0.47	0.57	0.58	0.82
15-30	0.52	0.58	0.60	0.93
30-45	0.54	0.59	0.61	0.93
45-60	0.62	0.60	0.61	0.93
60-80	0.63	0.60	0.57	0.90
80-100	0.64	0.63	0.57	0.89

In the study by Rhue et al., 1994, RPA for Quartzipsamment was correlated with clay content ($R^2 = 0.87$).

$$\text{RPA} = -10.076 + 128.769 \log (\text{clay} + 1)$$

Assuming that the relationship would apply to the soil at the study site and using the clay contents in (Table 2-3), the RPA for native soil should have been about 0.60 while that for the study site soil should have been about 0.45, showing the relative effect of clay content on RPA. Why these measured RPA values were higher than those predicted by the equation of Rhue et al., (1994) is not known. The effect of P loading on RPA has not yet been explored. The relative contribution of clay and P loading cannot be related from this data. The lower RPA values of the study site compared to the RPA values of the native site indicated lower relative P adsorption capacity of the study site. Single-point isotherm has been used to effectively index sandy materials. For example, Harris et al. (1996) stated that RPA effectively arrayed sandy Florida soil samples with respect to relative P adsorption. Their soil samples included five taxonomic groups for sandy surface and subsurface horizon groupings. The RPA values were 0.74 and 0.69 for A and Bt horizons of Paleudults, 0.54 for coated Quartzipsamments (defined as coated) in the surface horizon and 0.58 in the subsurface, 0.48-0.47 for uncoated Quartzipsamments (defined as slightly coated) surface and subsurface horizons, 0.26-0.08 for uncoated Quartzipsamments (defined as clean) surface and subsurface, and 0.05-0.01 for Alaquods surface and subsurface horizons, respectively. They also pointed out that RPA does not directly provide values for maximum P adsorption, but it closely relates to such values derived from P adsorption isotherms. Mozaffari and Sims (1994) also have evaluated single-point isotherms after Bache and Williams P sorption index (PSI) and indicated

that PSI may be a viable alternative to sorption isotherms for the purpose of a rapid means to assess the ability of a soil profile to retain additional P. The PSI in their case was found to be highly correlated ($r^2 = 0.94$) with the Langmuir P sorption maxima except when PSI exceeded 1400 mg/kg, where significant non-linearity was observed. Recently, Nair et al., (1998) found that single point sorption values measured at 1000 mg P/kg for soils of the Bh and Bw horizons from a low manure-impacted (pasture) and a high manure impacted (holding) areas were comparable ($r^2 = 0.98$) to the S_{\max} values calculated using a Langmuir equation and concluded that a single point sorption value was a very convenient and quick means of characterizing the soils for maximum P sorption capacity.

In this study, values of RPA for soil samples from the study site compared to the RPA values from a native site indicated clearly a low sorption capacity for the soil samples from the study site throughout the profile to 1m depth. The absence of significant differences in RPA values for different horizons within the profile could be due to the absence of differences in soil constituents known to be responsible for P sorption, such as clay content, between horizons within the profile. However, RPA values were correlated $r^2 = 0.65$ with double acid (Mehlich I)-extractable P, and Al (Table 4-2). Similarly, RPA also correlated with oxalate-extractable P, Al, and Fe ($r^2 = 0.63$, $n = 72$).

Degree of Phosphorus Saturation (DPS)

Degree of phosphorus saturation (DPS - 1) values of soil samples in the study site varied with depth in the soil profile. DPS - 1 indicated a 50% saturation in surface horizon, 26% at the 30-45 cm depth, 13-17 % at the 45-60 cm depth, and about 10-13% at lower depths of 80 and 100 cm pre-and post effluent application (Table 4-3). However,

Table 4-2. Multiple regression equations relating RPA to a) Mehlich I (DA) Al, Fe and P, b) Oxalate Al, Fe, and P in 1996 (prior to the application of effluent) (n = 72).

No.	Equation	Model R ²
a)	$RPA = 0.314 + 0.0022DA-Al^{***} + 0.01181 DA-Fe - 0.00021 DA-P^{***}$	0.65***
b)	$RPA = 0.515 + 0.0015 OX-Al^{***} - 0.00167 OX-Fe^{**} - 0.00087 OX-P^{***}$	0.63***

Table 4-3. DPS - 1[†] % values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native" soil (n = 1 profile). Values are Least Square Means (LSM).

Depth, cm	1996	1997	1998	Native
0-15	49.63	40.14	48.25	18.70
15-30	42.46	41.00	41.52	15.30
30-45	26.53	26.02	25.12	12.43
45-60	13.30	21.95	17.89	10.94
60-80	9.98	12.03	13.93	12.43
80-100	9.07	10.24	11.82	10.89

[†] $DPS - 1\% = (P_{ox} / (Fe_{ox} + Al_{ox})) \times 100$

the soil samples from native area adjacent to the study site showed DPS - 1 value of about 19% to 11% through out the soil profile (Table 4-3).

The DPS - 2 values for soil samples of the study area ranged from about 37% at the surface to 4% at a depth of 100 cm compared to 9% to 5% for soil samples from the native area, respectively (Table 4-4). Values of DPS - 1 and DPS - 2 for soil samples of the study area were highly correlated in strong relationship ($r^2=0.92$, $n = 144$) (Fig. 4-1). These results indicated that the surface horizon is more likely to release P than the deeper depths. Sharpley (1995) found that a P saturation of 25%, the critical value used in the Netherlands, would support a DP (Dissolved-P) concentration in surface runoff of 0.69 mg/L using Mehlich-3. Phosphorus sorption saturation, in his study, was calculated from Mehlich-3 extractable-P and Langmuir P-sorption maximum. However, in Florida, Mehlich I is the common soil P-test and the use of a common STP to express the DPS might be practically useful. If the DPS can be determined by a standard soil test procedure and commonly used as Mehlich I, the DPS can become a useful tool for evaluating and comparing areas of potential P losses. Also, the strong relationship between DPS - 1 and DPS - 2 suggested by this study, could be used to compare values of both DPS if this relationship is similar enough in other soils.

Langmuir Adsorption Parameters

Surface horizons from the study site prior to the application of effluent showed a lower Langmuir P- sorption maximum (55 mg/kg) associated with higher equilibrium P concentration (EPC_0) and a higher P originally sorbed (S_0) compared to subjacent horizons (Table 4-5). These differences were significant ($P<0.01$) for equilibrium P

Table 4-4. DPS - 2[†] % values within the soil profile of the study site (n = 12 profiles) prior and after to application of effluent compared to the "native" soil (n = 1 profile). Values are Least Square Means (LSM).

Depth, cm	1996	1998	Native
0-15	36.08	37.07	8.79
15-30	31.29	29.68	6.63
30-45	10.98	15.59	4.85
45-60	9.32	7.975	3.94
60-80	5.57	5.57	4.85
80-100	3.58	3.77	4.49

† DPS - 2 % = (Mehlich I extractable-P / (Fe_{ox} + Al_{ox})) x 100

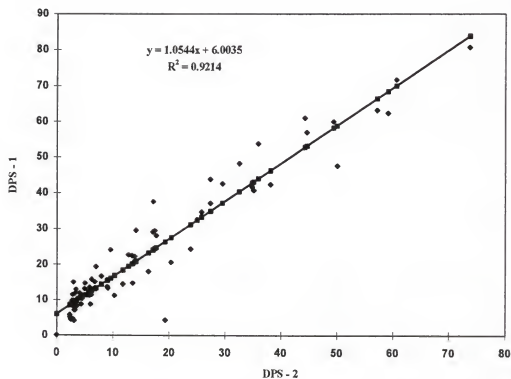


Figure 4-1. Relationship between Degree of P saturation (DPS - 1) calculated from oxalate extractable-P and Degree of P Saturation calculated from Mehlich I (DPS - 2) for soil samples from the study site.

Table 4-5. Comparison of Langmuir parameters (S_{\max} , EPC_0 , k) and S_0 mean values of different horizons within the soil profile prior to the application of effluent in 1996 and after two years of effluent application in 1998.

Year	Horizon	S_{\max} mg/kg	S_0 mg/kg	EPC_0 mg/L	k L/mg
<u>1996</u>	A 0-15cm	55 (13.2-76.3)	28.39a* (14.9-39.6)	8.81a (2.31-14.89)	0.15 (0.04-0.40)
	C1 30-45cm	100 (72.5-154)	5.16a (1.1-8.8)	1.19b (0.05-3.87)	0.37 (.048-0.64)
	C2 45-60 cm	95 (37-142.8)	4.23b (0-4.23)	0.79b (0-0.79)	0.54 (0.2-0.99)
<u>1998</u>	A 0-15 cm	88 (70.5-97.1)	25.63a (18.11-31.4)	5.02a (3.85-6.18)	0.12 (0.04-0.42)
	C1 30-45 cm	95 (27.7-153)	10.05b (2.29-25.8)	1.64b (0.5-4.0)	0.68 (0.07-2.8)
	C2 45-60 cm	96 (18.9-175)	4.67b (2.1-8.34)	0.57b (0.04-2.0)	0.74 (0.09-2.44)

* LS mean values for given parameters followed by the same letter are not significantly different ($p < 0.01$). Numbers in parentheses are the highest and lowest value for the parameter ($n = 18$).

concentration (EPC_0) and P originally sorbed (S_0). There were no significant difference in Langmuir parameters between 1996 and 1998. The same trend of a lower Langmuir P-sorption maximum associated with higher equilibrium P concentration (EPC_0) and a higher P originally sorbed (S_0) continued in 1998 after the application of effluent. The absence of differences in Langmuir parameters at the beginning and end of the study period could be attributed to the variability usually associated with such measurements, the study time limitation, and the fact that this site was heavily loaded with animal manure prior to the start of the study. However, equilibrium P concentration (EPC_0) showed a strong relationship ($r^2 = 0.94$) with $DPS - 1$ (Fig. 4-2). Based on this relationship, a $DPS - 1$ value of 20 % corresponds to an EPC_0 value of approximately 1 mg/L. Another parameter, from the isotherm study P_0 (P in solution after a 24-h equilibrium period when no P was added (soluble P)), also showed a strong relationship ($r^2=0.92$) with $DPS - 1$ (Fig. 4-3). Based on this relationship, a $DPS - 1$ value of 20% corresponds to a P_0 of approximately 5 mg/L. Such correlation between DPS and Langmuir parameters suggests that an integration of such tools could be used in the study of the assessment of the tendency of this soil to release P.

Summary and Conclusions

This study demonstrated the possibility of integrating a numbers of tools to characterize soil P retention at the study site. The use of a single point isotherm such as relative P adsorption (RPA) showed that the soil at the site has a lower relative adsorption for P compared to soils samples from a native site. After two years of effluent application, RPA values of soil samples from the study site did not show any significant change and remained in the same range reported before effluent application. The absence

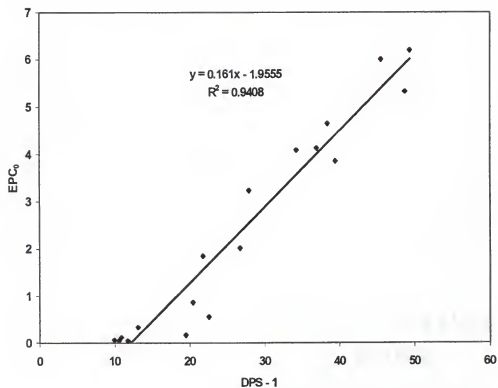


Figure 4-2. Relationship between Degree of P saturation calculated from oxalate extractable-P (DPS - 1) and equilibrium P concentration (EPC₀) for soil samples from the study site.

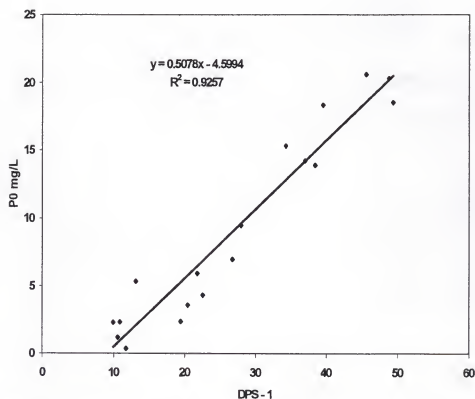


Figure 4-3. Relationship between Degree of P saturation calculated from oxalate extractable-P (DPS - 1) and soluble P (P₀) mg/L for soil samples from the study site.

of differences in RPA values pre-and post effluent application, indicated that effluent application did not influence P sorption capacity for this soil which has been heavily loaded with animal manure prior to the start of the study.

The degree of phosphorus saturation (DPS) showed that soil samples from the study site were 50% saturated at the surface compared to about 19% for the surface soil samples from the native site. These results indicated that the surface horizon is more likely to release P than the deeper horizons.

The isotherm study for this soil was also in agreement with the above finding where surface horizon showed a lower Langmuir P- sorption maximum (55 mg/kg) associated with higher equilibrium P concentration (EPC_0) and a higher P originally sorbed at the solid phase (S_0) compared to subjacent horizons. The same trend of a lower langmuir P- sorption maximum associated with higher equilibrium P concentration (EPC_0) and a higher P originally sorbed at the solid phase (S_0) continued in 1998 after the application of effluent, however no significant changes were observed between the two years.

Values of degree of P saturation (DPS - 1) and (DPS - 2) were highly correlated ($r^2 = 0.92$), which suggest the possibility of integrating the most common STP in the region (Mehlich I) into the useful approach of degree of P saturation. Also, DPS - 1 was highly correlated with equilibrium P concentration (EPC_0) ($r^2 = 0.94$), and with soluble P (P_0) ($r^2 = 0.92$). However, further research is needed to determine whether these relationships are similar enough in other sandy soils to be valuable as a tool in predicting the tendency of soil to release P.

CHAPTER 5

DOWNWARD PHOSPHORUS MOVEMENT ASSESSMENT IN A SANDY SOIL RECEIVING DAIRY WASTE EFFLUENT

Introduction

Loss of P from land can occur in three ways; as water-soluble and/or particulate P in surface runoff, as water-soluble and/or particulate P in subsurface runoff (leaching), and as water-soluble and/or particulate in flow to groundwater, referring to P picked up by water that passes to the water-table and which is subsequently discharged to streams, rivers or lakes as seepage (Ryden et al., 1973). P leaching has normally been considered to be inconsequential in most soils, but recent studies have found that there are a combination of agriculture management practices, soil properties, and climatic conditions that can result in significant P accumulation in subsoils. Whether or not P that leaches into subsurface horizons is later transported to water bodies depends on the depth of leaching and the hydrological connections of the watershed (Sims et al., 1998). The association of P accumulation with its downward movement has been the subject of numerous studies in soils amended with commercial fertilizers and /or organic wastes. Studies by King et al. (1990), Kingery et al. (1994), Mozaffari and Sims (1994), and Eghball et al. (1996) reported P leaching to ~75 cm depending on factors such as soil type and the amount of P accumulated in the surface horizon. Furthermore, Eghball et al. (1996) suggested a greater downward mobility for organic forms of P. Previous studies from Florida also illustrated the extent of P leaching that can occur in deep, sandy soils. One of the earliest studies in Florida was that of Bryan (1933) who reported P leaching to

depths of at least 90 cm in heavily fertilized citrus groves of varying ages. Humphreys and Pritchett (1971), in their study of six soil series in northern Florida, 6 to 10 years after applying superphosphate, reported extensive P leaching and subsequent accumulation in the spodic horizon of a Leon fine sand. They noted that all fertilizer P had leached below a depth of 50 cm in the Pomello and Myakka soil series. A study by Wang et al. (1994) found that high levels of P could be leached from surface (Ap) horizons of four sandy Florida soils heavily loaded with dairy manure despite high pH and abundant Ca^{2+} in solid and solution phases. Graetz and Nair (1995), Nair et al. (1995), Nair et al. (1998), and Nair et al. (1999), in a series of studies on Spodosols in the Lake Okeechobee basin of Florida, concluded that the P that leaves the surface (A) horizon might be lost through surface and subsurface drainage. The P portion that reaches the spodic (Bh) horizon will be held as Al- and Fe-associated P, either in the inorganic or in the organic fraction. The high percentage of HCl-extractable P (Ca- and Mg-associated P) in the A horizon of the intensive dairy component was also of potential concern. The HCl extractable P could be continuously extracted by NH_4Cl or by water (Graetz and Nair, 1995), suggesting that about 80% of the total soil P had the potential to move eventually with drainage water into Lake Okeechobee. Recently, Sims et al. (1998) reviewed current research on P leaching and loss in subsurface runoff in Delaware, Indiana, and Quebec. They concluded that the situation most commonly associated with extensive P leaching, and thus the increased potential for P loss via subsurface runoff, has been the long-term use of animal manures.

The most common soil P tests used to assess P status are the traditional agronomic soil tests for P such as Mehlich I, Mehlich 3, Bray I, and Olsen. These tests are often well

correlated with environmentally oriented P tests such as biologically available P (BAP) and dissolved reactive P (DRP) in runoff (Pote et al., 1996). Water soluble P (WSP) in particular has been characterized as an appropriate environmental soil P test (Sharpley et al., 1996, Moore et al., 1998). Therefore, this study was initiated to assess the vertical movement of P in the soil profile during application of dairy waste effluent to two cropping sequences in a deep sandy soil, using WSP and labile P concentrations within the profile as indicators of downward P movement.

Materials and Methods

Experiment Location and Design

The study site was located at North Florida Holstein Dairy facility, which is two miles south of Bell, Florida. A randomized block design containing three blocks and arranged as a split plot was used as the experimental design. Main plots were N loading rates and subplots were cropping systems. Subplot area was 232 m². Dairy waste effluent was used as the N source. The N application rates were 448 and 896 kg/ha/yr which correspond to P loading of 112 and 224 kg/ha/yr. The cropping systems were corn-forage sorghum-rye, and perennial peanut-rye.

Soil Selection and Sampling

The soil was mapped as Kershaw sand (sandy, thermic, uncoated Typic Quartzipsamments). Soil profile samples (0-15, 15-30, 30-45, 45-60, 60-80, 80-100 cm) were collected in 1996 (prior to effluent application) and in 1997, and 1998 (after effluent application). Soil from three profiles in each subplot was collected, composited, mixed thoroughly and a 1-kg subsample was brought to the laboratory for analysis. Soil samples were air-dried and sieved (2mm) prior to analysis. Soil samples were also collected in a

similar manner from an adjacent native area believed to be unimpacted by manure or fertilization application.

Soil Characterization

Texture was determined using the pipette method (Day 1965). Total phosphorus (TP) was determined by ashing 1.0 g of soil for 3 hours and then solubilizing with 6 M HCl (Anderson, 1976). Double-acid (Mehlich I)-extractable P, Al, Fe, Ca and Mg were obtained with a 1:4 soil/double acid ratio (Mehlich, 1953). Phosphorus (P) in solution was analyzed by the molybdenum-blue method (Murphy and Riley, 1962). Soil pH was determined on 1:2 soil/water ratio, and the organic carbon content of the air-dried samples was determined by combustion (Broadbent, 1965).

Water soluble P was extracted using a 1: 10 (soil: 0.01 M Ca Cl₂) ratio, by shaking the sample end- over-end for 1 hour, centrifuging for 20 min (1000 g), and filtering (0.45 µm). Phosphorus in solution was analyzed by the molybdenum-blue method (Murphy and Riley, 1962). Labile P was obtained using a fractionation scheme. The scheme used to fractionate soil-P was a modification by Nair et al. (1995) of that of Hietjes and Lijklema (1980). A 1-g air- dried sample was extracted twice with 25 mL of 1 M NH₄Cl (adjusted to pH 7.0) (two hours shaking). After each extraction, the content were centrifuged for 15 min at 3620 x g and filtered through a 0.45-µm filter. All extractions were carried out at room temperature. P determination was done using the procedure of Murphy and Riley (1962) on a spectrophotometer at wavelength of 880 nm. NH₄Cl-extractable P was defined as labile P (Pettersson and Istvanovics, 1988).

Statistical Analysis

Data analyses were done using SAS program (PROC MIXED) procedure (SAS Institute Inc. 1985). Relationships among parameters were evaluated using linear

correlation. Multiple regression was used to examine the strength of the relationships between parameters.

Results and Discussion

The soil from the study site showed a higher content of WSP prior to the application of effluent in 1996 compared to the WSP in the soil profile of the native soil collected from an adjacent site. WSP for soil samples from the study site ranged from 19.6 mg/kg at the surface to 1.9 mg/kg at 100 cm compared to 0.4 mg/kg at the surface and <0.1 mg/kg at lower depths of the native soil (Table 5-1). This higher content of WSP in the soil samples of the study site was associated with higher Mehlich I-extractable P as shown in (Table 5-2).

The effect of date*rate ($P < 0.001$), crop*rate ($P < 0.001$), and date*depth ($P < 0.001$) were significant for WSP. The application of effluent caused an increase in WSP content at all depths except the surface soil in 1998 and the change in WSP content was significant for both rates (Table 5-1). The high effluent application rate showed a decrease in the WSP content at the surface to about 30 cm then an increase down to the 100-cm depth (Table 5-3, Fig. 5-1). Similarly, WSP concentrations for the low effluent application rate increased at lower soil depths (Table 5-4, Fig. 5-2). However, though the trend of change in WSP content under the high and low rates effluent application at the surface horizon were similar, the trend of change in WSP under low rate application at the depths of 15-30, 30-45, and 45-60 cm was unexplainable. It was expected that such an increase in WSP concentrations at these soil depths would be acceptable for the high effluent rate application. Nevertheless, when WSP averages in all depths within the soil

Table 5-1. Mean water soluble P concentrations (WSP) in the soil profile prior to application of effluent (1996) and after application (1998) (n = 12 profiles) compared to native soil (n = 3 profiles). Values are least square means (LSM).

Depth (cm)	1996	1998	Native
		mg/kg	
0-15	19.6	13.9	0.4
15-30	16.2	22.2	0.1
30-45	9.10	23.2	<0.1
45-60	4.30	13.1	<0.1
60-80	2.80	8.10	<0.1
80-100	1.90	5.40	<0.1

Table 5-2. Mehlich I-extractable elements concentrations and total P (TP) in "native" soil (n = 1 profile) and study site soil profiles (n = 12 profiles) prior to the start of the study.

Location	Depth (cm)	Ca	Mg	Al mg/kg	Fe	P	TP
<u>Native</u>	0-15	11.7	1.9	267	18.4	47	214
	15-30	5.1	1.1	317	20.7	52	270
	30-45	6.0	0.8	330	19.1	39	241
	45-60	4.7	0.7	337	16.3	36	184
	60-80	4.7	0.8	308	16.3	39	181
	80-100	4.1	0.7	280	14.3	33	173
<u>Study Site</u>	0-15	968	115	301	23.5	283	328
	15-30	522	69.3	280	22.8	184	254
	30-45	208	34.1	203	19.6	75	154
	45-60	135	25.7	161	17.9	37	254
	60-80	103	22.9	133	15.9	20	218
	80-100	75	19.2	117	14.5	12	192

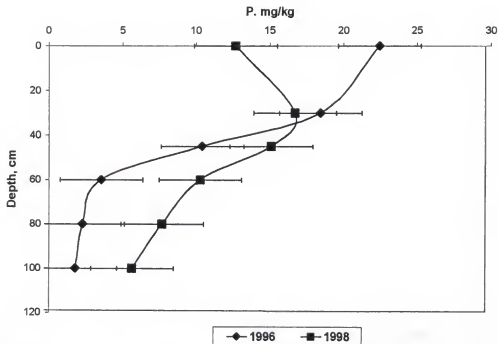


Figure 5-1. Mean water soluble P (WSP) concentrations within the soil profile of the study site under the high rate effluent application prior to the application of effluent in 1996 and after effluent application in 1998. Values are $LSM \pm Std. Error$.

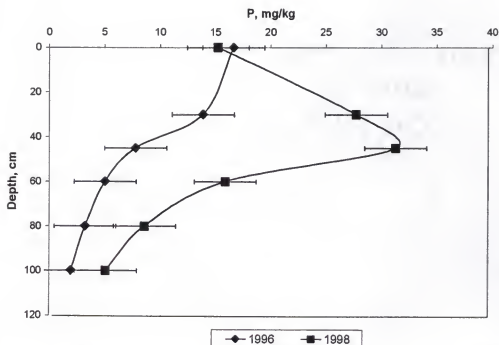


Figure 5-2. Mean water soluble P (WSP) concentrations within the soil profile of the study site under the low rate effluent application prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM \pm Std. Error.

Table 5-3. Changes in WSP concentration within the soil profile under high application rate after the application of effluent (1998) vs. prior to the application of effluent (1996).

Depth (cm)	1996 vs. 1998
0-15	-9.78**
15-30	NS
30-45	NS
45-60	NS
60-80	NS
80-100	NS

** Significant at the 0.001 probability levels, NS = none significant.

Table. 5-4. Changes in WSP concentration within the soil profile under the low application rate after the application of effluent (1998) vs. prior to the application of effluent (1996).

Depth (cm)	1996 vs. 1998
0-15	NS
15-30	13.8**
30-45	23.4**
45-60	10.8**
60-80	5.3**
80-100	NS

** Significant at the 0.001 probability levels, NS = none significant.

profile in 1998 was compared to those of 1996 (Fig. 5-3), it showed a trend similar to that found for Mehlich I-extractable P (Chapter 2). The trend may mimic vertical P movement in the soil profile and suggested that the decrease in the surface horizon may be attributed to both crop uptake of P and the leaching effect of effluent irrigation.

The labile P fraction or easily removable P as defined by (Pettersson and Istvanovics, 1988) behaved similarly to WSP regarding its increase in the lower depth of the profile. As mentioned in Chapter 3, a comparison of labile P mean concentrations in each depth within the soil profile at the beginning (1996) and end of the study period (1998) showed that the increase was statistically significant ($P < 0.001$ - $P < 0.05$) at all depths. Labile-P constituted 18-40% of TP in the soil profile. Labile-P in 1996 ranged from 85 in the surface horizon to 37 mg/kg at the lower depth (100 cm) which corresponded to 26 and 18% of TP, respectively. The application of effluent increased this fraction to 97 mg/kg in the surface horizon and 69 mg/kg at the lower depth (100 cm) in 1998. Labile-P increased at the surface horizon and throughout the profile over time with substantial increases in the lower depth accounting for 40% of TP in 1998 (Fig. 5-4). Previous research has shown that traditional agronomic soil P tests are often correlated with dissolved P and /or bioavailable P in runoff waters and subsurface drainage. Wolf et al. (1985) reported that the equilibrium P concentration at zero sorption (EPC_0) and algal-available P (extracted by a 0.1M NaOH + 1N NaCl solution) could be accurately predicted in a wide range of U.S. soils by the Bray P_1 , Mehlich 1, and Olsen soil P tests. Pote et al. (1996) also reported that water soluble P (WSP) was well correlated with runoff P in a field study with tall fescue.

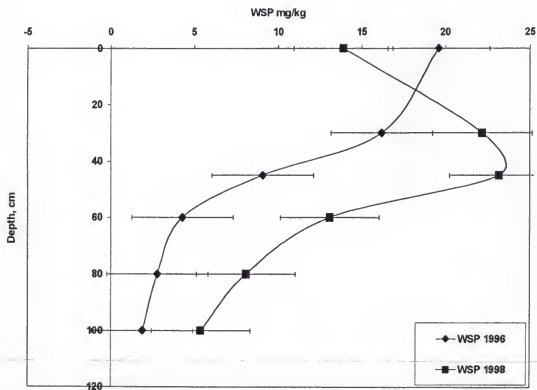


Figure 5-3. Mean water soluble P (WSP) concentration within the soil profile of the study site prior to the application of effluent in 1996 and after effluent application in 1998. Values are $LSM \pm Std. Error$.

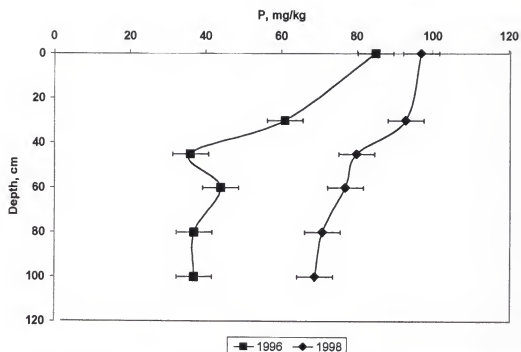


Figure 5-4. Labile-P concentration within the soil profile of the study site prior to the application of effluent in 1996 and after effluent application in 1998. Values are LSM \pm Std. Error.

In this study, a number of correlations were investigated to determine the strongest relationship between parameters. Labile P correlated with Mehlich I-P ($r^2 = 0.84$, $P < 0.001$) and WSP correlated with Mehlich I-P ($r^2 = 0.49$, $P < 0.001$) in 1996. The low r^2 value for WSP is due to high variability in WSP data. The significant relationships ($r^2 = 0.84$) between Mehlich I-P and labile P and Mehlich I-P and WSP ($r^2 = 0.49$) showed that Mehlich I-P is a good indicator of leachable P and/or P in the runoff. Pote et al. (1996) reported a significant relationship ($r^2 = 0.82$, $P < 0.001$) between WSP in surface soil and dissolved reactive P (DRP) in runoff and between Mehlich-3 in surface soil and dissolved reactive P (DRP) in runoff ($r^2 = 0.72$, $P < 0.001$).

The results of this study also showed a significant relationship between labile P and degree of phosphorus saturation. Labile P correlated with DPS - 2 ($r^2 = 0.71$, $P < 0.001$) and DPS - 1 ($r^2 = 0.62$, $P < 0.001$) in 1996. In contrast, WSP did not correlate as well as labile P with DPS - 1 ($r^2 = 0.57$, $P < 0.001$) and DPS - 2 ($r^2 = 0.49$, $P < 0.001$). These significant relationships between labile P and DPS and WSP and DPS showed the link between easily removable P and degree of P saturation. Pote et al. (1996) reported a significant relationship ($r^2 = 0.75$, $P < 0.001$) between DPS - 1 and dissolved reactive P (DRP) in runoff. The link between P concentration in soil solution and the degree of P saturation was suggested by Breeuwsma and Silva (1992), and results from the study site agree with this conclusion.

The correlation between labile P and DPS - 1 held true after two years of effluent application ($r^2 = 0.76$, $P < 0.001$), however in the case of labile P and DPS - 2, the correlation coefficient decreased to 0.23. In the case of WSP, there was also a decrease in correlation coefficient for DPS-1 ($r^2 = 0.13$) and DPS-2 ($r^2 = 0.22$). This trend was also

noted for the relationship between Mehlich I-P, labile P, and WSP. The correlation coefficients between labile P and Mehlich I-P was $r^2 = 0.31$ and between WSP and Mehlich I-P $r^2 = 0.12$. The results of the significant linear relationship between soil test P (Mehlich I), labile P and WSP, and labile P and WSP and DPS-1 and DPS-2 under the conditions of this study could be useful for future comparison with similar results of other soils. Downward (vertical) movement of P in this soil was suggested by both labile P and WSP data. During the two years of effluent application, both parameters showed either a decrease or a non significant change at the surface horizon, but a significant increase at the lower depths.

Summary and Conclusions

The association of P accumulation and downward movement has been the subject of numerous studies in soils amended with commercial fertilizers and/or organic wastes. Sims et al. (1998) indicated that the most common agricultural situation associated with significant downward movement of P has been the accumulation of P to "very high" or "excessive" levels in soils from continuous application of organic wastes.

Phosphorus leaching has normally been considered to be inconsequential in most soils but recent studies find that there are combinations of agriculture management practices, soil properties, and climatic conditions that can result in significant P accumulation in subsoils. Downward P movement in this soil was suggested by both labile P and WSP data. During the two years of effluent application, both parameters showed a significant increase at the lower depths of the soil profile. Phosphorus that leaches into subsurface horizons is later transported to water bodies depending on the depth of leaching and the hydrological connections of the watershed. Labile P increased

form 37 mg/kg at the start of the study to 69 mg/kg at 100 cm by the end of the study in 1998. Water soluble P showed a decrease at the surface horizon but increased in the lower depths of the soil profile by the end of the study period.

The results of the significant linear relationship between Mehlich I-extractable P and labile P ($r^2 = 0.84$), and Mehlich I-extractable P and WSP ($r^2 = 0.49$) 1996 could be useful for future comparison with similar results of other soils. If this relationship between soil test P (Mehlich I) and easily removable P proven to be valid for similar soils, it could be helpful in relating soil test P (Mehlich I) levels in soils to P movement within the soil profile.

Labile P and WSP also showed a significant relationships with DPS – 1 and DPS – 2 1996 which suggests a link between P concentration in soil solution and DPS reported by Breeuwsma and Silva (1992). The correlation between labile P and DPS – 1 held true ($r^2 = 0.76$) after two years of effluent application , but the other correlations decreased after two years of effluent application .

CHAPTER 6 UTILIZATION OF DAIRY WASTE EFFLUENT THROUGH SEQUENTIAL CROPPING

Introduction

Developing manure utilization plans that are agronomically, economically, and environmentally sound is a challenge. Issues like accelerated eutrophication, P or N limitation, transport mechanisms, source management, soil P level, environmental soil testing for P, and manure management have to be considered. Animal manure can be a valuable resource if it can be integrated into cost effective best management practices. However, the need for such plan supported by research, especially in areas of intensified dairy production and deep, sandy soil is urgent. Many factors may be involved in developing an environmentally sound plan for manure utilization management.

Uptake of nutrients by agronomic crop sequenced over time is an effective, economical, and environmentally sound means of nutrient recovery especially if the cropping system meets the environmental demand. The environmental demand can be met by maximizing nutrient uptake by the crops while meeting the need of dairy producers. Sweeten et al. (1995) reported that irrigation with dairy lagoon effluent enhanced forage quality yield and did not impair quality of runoff or vadose zone percolate under the conditions tested for two complete cropping years. Their cropping systems were summer-only coastal bermudagrass and a summer-winter coastal/wheat rotation. Land application of lagoon effluent at rates that were at or below soil test recommendations for total or available nitrogen resulted in runoff quality and vadose

zone percolate quality that were 94-99% lower in volatile solids, COD, N and P than concentration in the applied lagoon effluent.

A research report of two years of study on the use of dairy manure effluent in a rhizoma (perennial) peanut based cropping system (French et. al. 1995) suggested that if N pollution is the major concern in a particular area, then the PP-R (year-round perennial peanut and rye) would be a good choice since it performed as well or better than the C-FS-R (corn, forage sorghum, and winter rye) and C-PP-R (corn planted into a perennial peanut sod, perennial peanut, and rye) systems. However, if P were the major concern, the C-FS-R and C-PP-R systems would be better choices. The C-FS-R and C-PP-R systems were superior to the PP-R rotation in P removal values. Though P concentration level in perennial peanut forage were generally higher than those in corn and forage sorghum, they were not high enough to compensate for the much lower annual dry matter yield of the perennial peanut system.

This study was initiated to evaluate the effectiveness of the cropping systems, corn-forage sorghum-rye and perennial peanut-rye in P removal under two dairy waste effluent application rates.

Materials and Methods

Experiment Location and Design

The study site was located at the North Florida Holstein Dairy facility, which is two miles south of Bell, Florida. A randomized block design containing three blocks and arranged as a split plot was used as the experimental design. Main plots were N loading rates and subplots were cropping systems. Subplot area was 232 m². Dairy waste effluent

was used as the N source. The N application rates were 448 and 896 kg/ha/yr, which correspond to P loading of 112 and 224 kg/ha/yr.

Sampling and Analysis

Two cropping systems (corn-forage sorghum-rye and perennial peanut-rye) and two N application rates (448 and 896 Kg/ha/yr) which correspond to P loading of (112 and 224 Kg/ha/yr) respectively were sampled. The various crops were harvested at the appropriate times. In the corn-forage sorghum-rye (C-FS-R) system, corn was no-till planted into rye stubble and harvested in July. Forage sorghum was then no-till planted into existing corn stubble. Following sorghum harvest, rye was planted for the winter season using a no-till grain drill. For the perennial peanut-rye (P-R) system, the perennial peanut was harvested three times during the warm- growing season. Rye was overseeded into the peanut sod in late fall for the cool season crop.

Within each plot, a 9.3 m² portion was harvested, weighed and subsampled. Ground forage subsamples were sent to the Forage Evaluation Support Laboratory (FESL) at the University of Florida, Gainesville for analysis. Parameters measured include dry matter yield, N, and P concentration. N and P analysis involved a modification of the standard Kjeldahl procedure (Gallaher et al., 1975), followed by automated colorimetry (Hambleton, 1977) using a Technicon Auto Analyzer.

The data and the statistical analysis were provided by Woodard et al. (2000) and are used herein to relate crop uptake to P accumulation in the soil. Responses were analyzed by fitting mixed effect models using the PROC MIXED procedure of SAS (SAS Institute Inc., 1992) and years were considered as repeated measures.

Results and discussion

Mean P removal in the 1996-97 and the 1997-98 seasons from the corn-forage sorghum-rye (C-FS-R) cropping system was significantly higher compared to the perennial peanut-rye cropping system (Fig. 6-1 and 6-2). Mean P removal in the 1996-97 season from the corn-forage sorghum-rye (C-FS-R) cropping system was the highest 67.2 kg/ha (Table 6-1) compared to the perennial peanut-rye cropping system (Table 6-2). Mean P removal in (1997-98) season for the corn-forage sorghum-rye (C-FS-R) cropping system accounted for about 62 kg P/ha (Table 6-1) with no significant difference in P removal between 1996-97 and 1997-98 seasons. However, the perennial peanut-rye cropping system removed only about 35-39 kg P/ha in (1996-97) season and 45-54 kg/ha in (1997-98) season (Table 6-2). The higher P removal of the corn-forage sorghum-rye cropping system than perennial peanut-rye was reflected in the soil data reported in Chapter 2. Mehlich I-extractable P concentrations in soil from perennial peanut-rye cropping system plots was higher than those of the corn-forage sorghum-rye. This difference in Mehlich I-extractable P concentrations was significant ($P < 0.05$) under the high application rate.

The difference in dry matter yield between the cropping systems was significant in both seasons (Woodard et al., 2000). Dry matter yield of the corn -forage sorghum-rye cropping system was 27 Mg/ha in both seasons (Table 6-3), while the perennial peanut-rye cropping system dry matter yield was 12 Mg/ha in 1996-97 season and 18 Mg/ha in the 1997-98 season (Table-6-4).

The effect of effluent application rate/year on P removal of the corn-forage sorghum-rye was not significant for both seasons, while the effect of effluent application

Table 6-1. P removed (kg/ha) by the corn-forage sorghum-rye cropping system under high and low application rates during the 1996-97 and 1997-98 seasons. (Data obtained from Woodard et al. 2000).

Application rate	Corn	Forage sorghum	Rye	Total
	kg/ha			
	<u>1996-97</u>			
High	30.2	17.9	16.8	65
Low	32.5	19.0	15.7	67
	<u>1997-98</u>			
High	31.4	17.9	14.6	64
Low	31.4	19.0	10.0	60

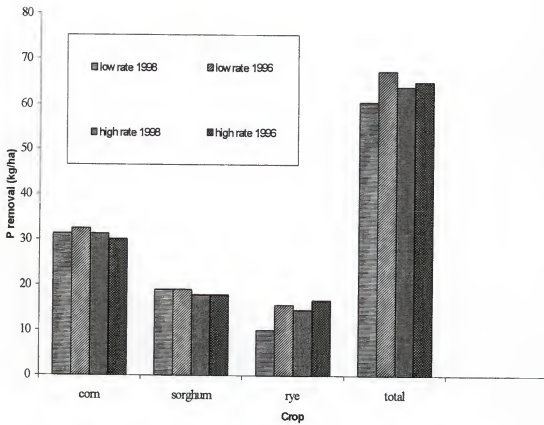


Figure 6-1. P removal (kg/ha) of corn-forage sorghum-rye during the 1996-97 and 1997-98 seasons.

Table 6-2. P removed (kg/ha) by the perennial peanut-rye cropping system under high and low application rates during the 1996-97 and 1997-98 seasons. (Data obtained from Woodard et al. 2000).

Application rate	P.peanut			Rye kg/ha	Total
<u>1996-97</u>					
	<u>1st</u>	<u>2nd</u>	<u>3rd</u>		
High	9	8	-	18	35
Low	8	8	-	23	39
<u>1997-98</u>					
	<u>1st</u>	<u>2nd</u>	<u>3rd</u>		
High	13	15	07	19	56
Low	13	15	07	10	54

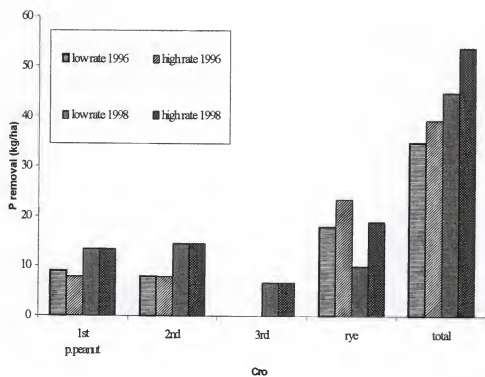


Figure 6-2. P removal (kg/ha) of perennial peanut-rye during the 1996-97 and 1997-98 seasons.

rate/year on P removal of the perennial peanut-rye was significant in both seasons (Woodard et al., 2000). The average removal of P for forage crops in this study, including perennial peanut in the second season, were in agreement with the reported P removal for such crops by French et al. (1995), and published book value (NRCS Manure Master, 1999). However, despite the higher P removal by the C-FS-R than the P-R cropping system, P removal by the cropping system did not alter the high level of the soil P that was already present before application of the effluent (Chapter 2). After a high level of soil test P has been attained, considerable time is required for significant P depletion as reported by McCollum (1991).

Summary and Conclusions

Uptake of nutrients by agronomic crops sequenced over time is an effective, economical, and environmentally sound means of nutrient recovery. Cropping systems are needed to maximize nutrient uptake while meeting the needs of dairy producers. In this study, higher P removal was recorded for the corn-forage sorghum-rye in both seasons. The higher P concentration in dry matter of perennial peanut and rye was not high enough to offset the lower dry matter yield. The perennial peanut-rye cropping system removed less P than corn-forage sorghum-rye cropping system. However, despite the higher P removal by C-FS-R than the P-R cropping system, P removal by the cropping system did not alter the high level of soil P that was already present before application of the effluent. After a high level of soil test P have been attained, considerable time is required for significant P depletion. Further investigation is needed to determine the best application rate based on N or P after taking in consideration the

Table 6-3. Average dry matter yield of the corn-forage sorghum-rye during the 1996-97 and 1997-98 seasons.

Crop	Dry matter yield (Mg/ha)	
	<u>1996-97</u>	<u>1997-98</u>
Corn	15	12
Forage sorghum	08	11
Rye	04	04
Total	27	27

Table 6-4. Average dry matter yield of the perennial peanut-rye during the 1996-97 and 1997-98 seasons.

Crop	Dry matter yield (Mg/ha)	
	<u>1996-97</u>	<u>1997-98</u>
P. Peanut	07	13
Rye	05	05
Total	12	18

soil P that was already present in the soil before application, and the needs of dairy producers.

CHAPTER 7 SUMMARY AND CONCLUSIONS

The study site soil was mapped as Kershaw sand (sandy, thermic, uncoated Typic Quartzipsamments) in the Gilchrist County soil survey report (Soil Survey Staff, Gilchrist County, Florida, 1973). Since the publication of the report, the criterion for coated vs. uncoated family placement has been changed for the USDA soil taxonomic system (Soil Survey Staff, 1999). The sandy materials sampled in this study would meet the criterion for coated family (5 percent silt plus 2 times the clay content), based on the particle size analysis. Also, some auger borings to 2 m revealed spodic horizons which indicated inclusions of Spodosols, and dark colors in the surface horizon in some areas qualify it to be an Umberic epipedon, which would result in classification as an Inceptisol (Umbrept) rather than a Psamment. Nevertheless, the soil was consistently sandy and similar to Kershaw with respect to use and management.

Loss of P from land can occur in three ways; as water-soluble and/or particulate P in surface runoff, as water-soluble and/or particulate P in subsurface runoff (leaching), and as water-soluble and/or particulate P in flow to groundwater, referring to P picked up by water that passes to the water-table and which is subsequently discharged to stream, rivers or lakes as seepage (Ryden et al., 1973). P leaching has normally been considered to be inconsequential in most soils, but recent studies find that there are combinations of agriculture management practices, soil properties, and climatic conditions that can result in significant P accumulation in subsoils. Whether or not P that leaches into subsurface horizons is later transported to water bodies depends on the depth of leaching and the

hydrological connections of the watershed (Sims et al., 1998). However, the most common agricultural situation associated with significant downward movement of P has been the accumulation of P to "very high" or "excessive" levels in soils from continuous application of organic wastes (manure, litter, and municipal or industrial wastes and waste waters) (Sims et al., 1998). The trend of P accumulation and leaching has also been shown in Florida, which has intensive agricultural activity, humid climate, frequent heavy rainfall, and widespread use of irrigation and drainage. Several studies have shown the extent of P leaching that can occur in deep, sandy soils.

In 1990, the Middle Suwannee River area was approved as a Hydrologic Unit Area project based on data generated by the Florida Department of Environmental Protection. These data showed an elevated concentration of nitrate-nitrogen in the Floridan Aquifer in the Suwannee River Basin, especially in areas of intensive agricultural activity. Phosphorus concentrations in the Suwannee River ranged from 0.40 to 0.49 mg/L which were 6.4 times the median regional value of north Florida streams. The Hydrologic Unit Area program was developed to reduce or prevent water quality degradation of the Floridan Aquifer and the Suwannee River resulting from agricultural operations. Management of nutrients (potential contaminants) in dairy waste effluent through spray field crop production systems is an important component in the overall scheme for protecting ground and surface water from elevated levels of N and P. The use of inappropriate crop management technology under a dairy effluent irrigation system can lead to the loss of N to the ground water. Uptake of nutrients by agronomic crops sequenced over time is an effective, economical, and environmentally sound means of

nutrient recovery. Cropping systems designs are needed to meet environmental demands by maximizing nutrient uptake while meeting the needs of dairy producers.

The Use of Dairy Manure Effluent in A Rhizoma (Perennial) Peanut Based Cropping Systems for Nutrient Recovery and Water Quality Enhancement was a research project established under the Hydrologic Unit Area project (HUA). The objective of this project was to evaluate five cropping systems grown under a dairy effluent disposal irrigation system, comparing their effectiveness in nutrient recovery and maintenance of acceptable levels of N and P in ground water. The cropping systems were corn-forage sorghum-rye, corn-bermuda grass-rye, bermuda grass-rye, perennial peanut-rye, and corn-perennial peanut-rye and the N application rates were (448,672 and 896 kg/ha/yr) which correspond to P loadings of (112, 168 and 224 kg/ha/yr). My study was a component of this project and addressed P forms and retention in the soil profile under two cropping systems (corn-forage sorghum-rye and perennial peanut-rye) and two N application rates (448 and 896 kg/ha/yr) which correspond to phosphorus loadings of (112 and 224 kg/ha/yr). The corn-forage sorghum-rye cropping system represents traditional crops for the Middle Suwannee River area and the perennial peanut-rye system is an improved cropping system recently introduced to the area.

The main objective of this research was to study the effect of dairy waste effluent application on P accumulation, forms, and retention in the soil profile of a sandy soil under two cropping systems. The specific objectives and hypotheses of this research were as follows:

Objective 1: Quantify and characterize inorganic P forms in the soil profile of the chosen cropping systems with increasing effluent P application.

Hypothesis: Application of dairy effluent will increase P levels in the soil resulting in an accumulation of P in the soil profile.

Objective 2: Quantify and characterize P retention in the soil profile.

Hypothesis: Soil retention capacity will decrease with continuous addition of dairy effluent and may induce a downward movement of P.

Objective 3: Determine P uptake by the chosen cropping systems under two rates of effluent application.

Hypothesis: P accumulation in soil profile will decrease with increasing plant uptake.

The effect of effluent application on P accumulation was discussed in Chapter 2. Phosphorus forms and fractionation data are presented in Chapter 3 while P retention was discussed in Chapter 4. Downward P movement was assessed in Chapter 5 and P removal by the cropping systems was presented in Chapter 6. In this chapter, the most important finding of this research are summarized according to the objectives and hypotheses mentioned above. In addition, future research topics are identified.

Investigation of the P levels at the study site indicated that the soil appears to have been heavily loaded with animal waste prior to the start of this study, although amounts and dates could not be established. The application of dairy effluent during the study period resulted in increased TP level through out the soil profile. Soil test P (Mehlich I) increased for the P-R cropping system under the high application rate. Soil test P (Mehlich I) was highly correlated with Ca, Mg, Al and Fe extracted by Mehlich I solution, with 93% of the variability explained by this relationship.

Al- and Fe-associated P constituted the major proportion (62%) of the TP in the soil profile. Labile-P constituted 18 to 40% of TP throughout the profile with an increasing trend at the lower depth of the soil profile by the end of the study period. Labile P is defined as easily removable P and its increase in the lower depths is a clear indication of a vertical P movement. In fact, the application of dairy effluent during the study period increased all P pools significantly throughout the soil profile except Ca- and Mg-associated P which remained constant.

The ability of the soil at the study site to retain P was low in comparison to soil from the native site. The relative P adsorption (RPA) for the study site soil was 0.5 to 0.6 while the native soil RPA was 0.8 to 0.9. The lower retention of P for this soil was associated with about 50% P saturation at the surface soil. The Degree of P Saturation (DPS) for the surface soil from the native site was about 17%. Higher DPS values for the surface soil suggests that the surface horizon is more likely to release P than the deeper soil depths. Degree of P Saturation showed a strong relation with EPC_0 and P_0 which suggests that DPS can be used in the assessment of the tendency of this soil to release P. Downward P movement in the soil profile suggested by water soluble phosphorus (WSP) and labile P data. Both parameters, during the two years of effluent application showed a significant increase in the lower soil depths.

Phosphorus removal by the cropping systems was higher for the C-FS-R than the P-R cropping system. However, P uptake by the cropping systems did not reduce the high level of soil P that was already present before effluent application. This study suggests that when STP levels in the soil exceed optimum values for crop production, the

application of dairy waste based on estimated crop N requirements may not be appropriate on heavily P loaded sandy soil such as at the study site.

Further research is needed in the area of linking traditional soil test P with environmentally oriented P tests such as WSP. The results of the significant linear relationship between soil test P (Mehlich I), labile P and WSP, and labile P and WSP and DPS-1 and DPS-2 under the conditions of this study could be useful for future comparison with similar results of other soils. Also, DPS is another area for future research. Values of DPS - 1, calculated from oxalate extractable-P and DPS - 2, calculated from Mehlich I for soil samples from the study site were highly correlated ($r^2 = 0.92$) which suggest the possibility of integrating the DPS to the most common soil test P in the region. Other correlations, such as equilibrium P concentration (EPC_0) and DPS - 1 ($r^2 = 0.94$), and soluble P (P_0) and DPS - 1 ($r^2 = 0.92$) suggest that an integration of such tools could be used in the study of the assessment of the tendency of this soil to release P.

APPENDIX

SELECTION OF SOIL: SOLUTION RATIO

The solid: solution ratio is critical in sequential extraction. The use of excess solid can result in incomplete dissolution of target phases due to saturation of the solution with respect to the target phase (Ruttenberg 1990). A modification for solid: solution is always needed for a specific sample (Ruttenberg 1992). Therefore, prior to the selection of the soil: solution ratio used in this study, three soil samples from the study site were used for comparison with three different soil: solution ratios. The soil samples (1c, 3c, and 6c) were from three different depths; 0-15, 30-45, and 80-100 cm, respectively. The soil: solution ratio tried were; 1/10, 1/25, and 1/50. All samples were subjected to a complete fractionation scheme, as explained below, with two modified procedures. The first, include the complete procedure with three 1 M NH_4Cl (adjusted to pH 7.0) extractions, and the second include the complete procedure with one 1 M NH_4Cl (adjusted to pH 7.0) extractions.

In a third trial, the same soil samples were subjected to a complete fractionation scheme with two soil: solution ratios (1/50 and 1/100) and three 1 M NH_4Cl (adjusted to pH 7.0) extractions. Total P (TP) for the three samples used in these trials were determine by ashing 1.0 g of soil for 3 hours and then solubilizing with 6 M HCl (Anderson, 1976). Their TP were 816, 304, and 111, respectively.

The preliminary data of the two trials were shown in the tables (3-1, 3-2, and 3-3) below. A careful examination of the data in term of P concentration in each trial and

extraction suggested that the 1/25 soil: solution ratio and two 1 M NH_4Cl (adjusted to pH 7.0) extractions seem to be appropriate for this soil.

Table 1-1. Data of trial (1), soil: solution ratio selection

Sample	Ratio	NH_4Cl 1	NH_4Cl 2	NH_4Cl 3	NaOH	HCl
P (mg/kg)						
1c	1/10	14	16	16	551	277
1c	1/10	14	16	16	581	272
1c	1/25	24	13	17	654	93
1c	1/15	24	24	17	804	90
1c	1/50	21	22	18	566	76
1c	1/50	23	18	10	561	74
3c	1/10	6	4	9	219	138
3c	1/10	6	4	4	216	133
3c	1/25	9	1	5	353	29
3c	1/15	7	2	1	338	36
3c	1/50	4	0	1	323	38
3c	1/50	4	0	0	309	34
6c	1/10	0	0	0	88	17
6c	1/10	0	0	0	84	18
6c	1/25	0	0	0	86	22
6c	1/15	0	0	0	94	22
6c	1/50	0	0	0	105	32
6c	1/50	0	0	0	97	31

Table 1-2. Data of trial (2), soil: solution ratio selection

Table 1-2. Data of trial (2), soil: solution ratio selection				
Sample	Ratio	NH ₄ Cl 1	NaOH	HCl
		P (mg/kg)		
1c	1/10	15	207	584
1c	1/10	15	566	241
1c	1/25	27	599	325
1c	1/15	26	746	260
1c	1/50	22	596	97
1c	1/50	23	659	102
3c	1/10	7	333	71
3c	1/10	7	319	90
3c	1/25	10	380	41
3c	1/15	3	384	40
3c	1/50	0	356	39
3c	1/50	0	385	36
6c	1/10	0	63	29
6c	1/10	0	93	16
6c	1/25	0	89	22
6c	1/15	0	88	21
6c	1/50	0	115	33
6c	1/50	0	111	30

Table 1-3. Data of trial (3), soil: solution ratio selection

Sample	Ratio	NH ₄ Cl 1	NH ₄ Cl 2	NH ₄ Cl 3	NaOH	HCl
		P (mg/kg)				
1c	1/50	49	39	28	610	47
1c		49	36	26	602	44
3c		31	20	14	432	23
3c		29	19	15	388	19
6c		4	4	4	126	12
6c		4	4	4	118	12
1c	1/100	70	51	27	695	54
1c		77	49	33	374	218
3c		42	29	19	415	21
3c		37	24	19	398	20
6c		7	7	6	145	12
6c		7	7	6	143	13

LIST OF REFERENCES

- American Public Health Association (APHA). 1985. Standard Methods for the Examination of water and Wastewater, 16th ed., Washington, DC: American Public Health Association.
- Anderson, J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. *Water Res.* 10:329-331.
- Bache, B. W., & E.G. Williams. 1971. A phosphate sorption index for soils. *J. Soil Sci.* 22:289-301.
- Barnhisel, R., & P.M. Bertsch. 1982. Aluminum. In A.L. Page, R.H. Miller, & D.R. Keeney (eds.), *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties*, 2nd ed. Madison, WI: ASA/SSSA.
- Beegle, Douglas, Andrew Sharpley, & Don Graetz. 1998. Interpreting soil test phosphorus for environmental purposes. In J. Thomas Sims (ed.), *Soil Testing for Phosphorus: Environmental Uses and Implication*. SERA-IEG 17 USDA-CREES Regional Committee: Minimizing Agricultural Phosphorus Losses for protection of the Water Resources. Bulletin No. 389.
- Boggess, C.F., E.G. Flaig, & R.C. Fluck. 1995. Phosphorus budget-basin relationships for Lake Okeechobee tributary basin. *Ecol. Eng.* 5:143-162.
- Bowman, R.A., Rodriguez, J.B. and Self, J.R. 1998. Comparison of methods to estimate occluded and resistant soil phosphorus. *Soil Sci. Soc. Am. J.* 62:338-342.
- Brady, N.C. 1990. *The Nature and Properties of Soil*. 10th ed. Upper Saddle River, NJ: Prentice-Hall.
- Breeuwsma, A., J.G.A. Reijerink, & O.F. Schoumans. 1995. Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. P. 239-251. In K. Steele (ed.), *Animal waste and the land-water interface*. New York: Lewis Publishers-CRC.
- Broadbent, F.E. 1965. Organic Matter. In Black, C.A ed., *Methods of Soil Analysis*, Part 2, pp. 539-580.
- Chang, S.C., & M.L. Jackson. 1957. Fractionation of soil phosphorus. *Soil Sci.* 84:133-144.

- Copee, J.T., C.E. Evans, & H.C. Williams. 1981. Soil test fertilizer recommendations for Alabama crops. Alabama Agric. Exp. Stn. Circ. 251.
- Daniel, T.C., A.N. Sharpley, & J.L. Lemunyon. 1998. Agriculture phosphorus and eutrophication: A symposium overview. *J. Environ. Qual.* 27:251-257.
- Dantzman, C.L., M.F. Richter, and F.G. Martin. 1983. Chemical elements in soils under cattle pens. *J. Environ. Qual.* 12:164-168.
- Day, P.R. 1965. Pipette method of Particle Size Analysis. In C.A. Black (ed.). *Methods of Soil Analysis, Part 1 Agronomy*. 9: 552-562. Amer. Soc. of Agron, Madison, WI.
- Dooley, D.O. 1996. The status of phosphorus in natural wetland receiving dairy lagoon effluent. MS. Thesis. University of Florida, Gainesville.
- Dooley, D.O., V.D. Nair, & D.A. Graetz. 1993. Phosphorus release from beef and dairy manures and manure-contaminated soils. P.29. In *agronomy abstracts*. Madison, WI: ASA.
- Eghball, B., G.D. Binford, & D.D. Baltensperger. 1996. Phosphorus movement and adsorption in a soil receiving long-term manure and fertilizer application. *J. Environ. Qual.* 25:1339-1343.
- Federico, A., K.G. Dickson, C.R. Kratzer, & F.E. Davis. 1981. Lake Okeechobee water quality studies and eutrophication assessment. Tech. Publ. 81-2. West Palm Beach, FL: South Florida Water Management District.
- French, E.C., K.R. Woodard, D.A. Graetz, G.M. Prine, & H.H. Van Horn. 1995. A second year report on the use of dairy manure effluent in a rhizoma (perennial) peanut based cropping system for nutrient recovery and water quality enhancement. In *Proc. 32nd Annual Florida Dairy Production Conference*. 11-12 April 1995. Gainesville: University of Florida, Gainesville, FL.
- Graetz, D.A. 1989. Phosphorus levels in soils of selected Lake Okeechobee watershed dairies. P. 113-118. In *Proc. 26th Annual Florida Dairy Production Conference*. 2-3 May 1989. Gainesville: University of Florida.
- Graetz, D.A., & V.D. Nair. 1995. Fate of phosphorus in Florida spodosols contaminated with cattle manure. *Ecol. Eng.* 5:163-181.
- Graetz, D.A., & V.D. Nair. 1999. Inorganic forms of phosphorus in soils and sediments. pp 171-182. In K. R. Reddy, G. A. O'Connor, & C.L. Schelske (eds.) *Phosphorus Biogeochemistry in Subtropical Ecosystems*. Boca Raton, FL: CRC Press.

- Graetz, D.A., V.D. Nair, & K.R. Reddy. 1991. Biogeochemical behavior and transport of phosphorus in the Lake Okeechobee Basin. South Florida Water Management District, West Palm Beach, FL.
- Harris, W.G., R.D. Rhue, G. Kidder, R.B. Brown, & R. Littell. 1996. Phosphorus retention as related to morphology of sandy coastal Plain materials. *J. Environ. Qual.* 60:1513-1521.
- Harris, W.G., H.D. Wang, & K.R. Reddy. 1994. Dairy manure influence on soil and sediment composition: implication for phosphorus retention. *J. Environ. Qual.* 23:1071-1081.
- Harris, Willie, & Wade Hurt. 1999. Introduction to soils of subtropical Florida. pp 143-162. In K. R. Reddy, G. A. O'Connor, & C.L. Schelske (eds.), *Phosphorus Biogeochemistry in Subtropical Ecosystems*. Boca Raton, FL: CRC Press.
- Hietjes, A.H.M., & L. Lijklema. 1980. Fractionation of inorganic phosphate in calcareous sediments. *J. Environ. Qual.* 9:405-407.
- King, L.D., J.C. Burns, & P.W. Westerman. 1990. Long-term swine lagoon effluent application on coastal bermuda grass: II. Effect on nutrient accumulation in soil. *J. Environ. Qual.* 19:756-760.
- Kingery, W.L., C.W. Wood, D.P. Delaney, J.C. Williams, & G.L. Mullins. 1994. Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.* 23:139-147.
- Lanyon, L.E. 1994. Dairy manure and plant nutrient management issues affecting water quality and the dairy industry. *J. Dairy Sci.* 77:1999-2007.
- Lemunyon, J., & T.C. Daniel. 1998. Phosphorus management for water quality protection: A national effort. In J. Thomas Sims, (ed.), *Soil Testing for Phosphorus: Environmental Uses and Implication*. SERA-IEG 17 USDA-CREES Regional Committee: Minimizing Agricultural Phosphorus Losses for protection of the Water Resources. Bulletin No. 389.
- Manure Master. 1999. <http://netral.ftw.nrcs.usda.gov/ManureMaster/MM22.html>
- McKeague, J.A., & J.H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46:13-22.
- Mehlich, A. 1953. Determination of p, Ca, Mg, K, Na and NH_4 . Soil Testing Div. Publ. 1-53, Raleigh, NC: North Carolina Department of Agriculture.
- Menzies, N.W., J.A. Skilton, & C.N. Guppy. 1999. Phosphorus storage on effluent irrigated land. *J. Environ. Qual.* 28:750-754.

- Moore, Phillip A. Jr., Brad C. Joern, & Tony L. Provin. 1998. Improvrmnt needed in environmental soil testing. In Sims, J. Thomas (ed.) *Soil Testing for Phosphorus: Environmental Uses and Implication*. SERA-IEG 17 USDA-CREES Regional Committee: Minimizing Agricultural Phosphorus Losses for protection of the Water Resources. Bulletin No. 389.
- Mozaffari, M., & J.T. Sims. 1994. Phosphorus availability and sorption in an Atlantic Coastal Plain watershed dominated by animal based agriculture. *Soil Sci.* 157:97-107.
- Mozaffari, M., & J.T. Sims. 1996. Phosphorus transformation in poultry litter-amended soils of the Atlantic Coastal Plain. *J. Environ. Qual.* 25:1357-1365.
- Murphy, J., & J.P. Riely. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31-36.
- Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, & T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. *J. Environ. Qual.* 13:591-595.
- Nair, V.D., D.A. Graetz, & K.M. Portier. 1995. Forms of phosphorus in soil profile from dairies of South Florida. *J. Environ. Qual.* 59:1244-1249.
- Nair, V.D., D.A. Graetz, & K.R. Reddy. 1998. Dairy manure influences on phosphorus retention capacity of Spodosols. *J. Environ. Qual.* 27:522-527.
- Nair, V.D., R.R. Villapando, & D.A. Graetz. 1999. Phosphorus retention capacity of Spodic horizon under varying environmental conditions. *J. Environ. Qual.* 28:1308-1313.
- Olsen, S.R. & F.E. Khasawneh. 1980. Use and limitation of physical-chemical criteria for assessing the status of phosphorus in soils. pp. 361-410. In F.E. Khasawneh, E.C. Sample & E.J. Kamprath (eds.), *The Role of Phosphorus in Agriculture*. Madison, WI: SSSA.
- Olsen, S.R., & L.E. Sommers. 1982. Phosphorus. In A.L. Page, R.H. Miller & D.R. Keeney (eds.), *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties*, 2nd ed. Madison, WI: ASA/SSSA.
- Parry, R. 1998. Agricultural phosphorus and water quality: A U. S. Environmental Protection Agency perspective. *J. Environ. Qual.* 27:258-261.
- Pettersson, K., & V. Istvanovics. 1988. Sediment phosphorus in Lake Balaton: Forms and Mobility. *Ergeb. Limnol.* 30:25-41.

- Pote, D.H., T.C. Daniel, A.N. Sharpley, P.A. Moore, Jr., D.R. Edwards, & D.J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60:855-859.
- Project C-2: Use of Dairy Manure Effluent in a Rhizoma (Perennial) Peanut Based Cropping System for nutrient Recovery and Water Quality Enhancement. 1995, Gainesville:IFAS, University of Florida.
- Reddy, K.R., E.G. Flaig, & D.A. Graetz. 1996. Phosphorus storage capacity of uplands, wetlands and streams of the Lake Okeechobee Watershed, Florida. *Agriculture, Ecosystems and Environment* 59: 203-216.
- Reddy, K.R., E. Lowe, & T. Fontaine. 1999. Phosphorus in Florida's ecosystems: analysis of current issues. pp 111-138. In K. R. Reddy, G. A. O'Connor, & C.L. Schelske (eds.) *Phosphorus Biogeochemistry in Subtropical Ecosystems*. Boca Raton, FL: CRC Press.
- Reddy, K.R., G.A. O'Connor, & P.M. Gale. 1998. Phosphorus sorption capacities of wetland soils and sediments impacted by dairy effluent. *J. Environ. Qual.* 27:438-447.
- Rhue, R.D. & Willie G. Harris. 1999. Phosphorus sorption/desorption reactions in soils and sediments. pp 187-203. In K. R. Reddy, G. A. O'Connor, & C. L. Schelske (eds.), *Phosphorus Biogeochemistry in Subtropical Ecosystems*. Boca Raton, FL: CRC Press.
- Rhue, R.D., W.G. Harris, G. Kidder, R. B. Brown, and R. C. Brown. 1994. A soil-based phosphorus retention index for animal waste disposal on sandy soil. Final Project Report. Florida Department of Environmental Protection, Tallahassee, FL.
- Ruttenberg, Kathleen C. 1990. Diagenesis and burial of phosphorus in marine sediments: Implication for the marine phosphorus budget. Ph.D. thesis, Yale Univ. 375p.
- Ruttenberg, Kathleen C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 37(7):1460-1482.
- Ryden, J.C., & J.K. Syers. 1977. Origin of the labile phosphate pool in soils. *Soil Sci.* 123:353-361.
- SAS Institute Inc. 1985. *SAS User's Guide: Statistics*, Version 5th. Ed. Cary, NC: SAS.
- Schabenberger, Oliver. 1996. A Brief Comparison of PROC GLM and PROC MIXED of SAS. <http://www.cas.vt.edu/schabenb/GLMvsMIXED.html>

- Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., Daniel, T.C. & Reddy, K.R. 1994b. Managing agricultural phosphorus for protection of surface waters: issues and options. *J. Environ. Qual.* 23:437-451.
- Sharpley, A.N., & A.D. Halvorson. 1994. The management of soil phosphorus availability and its impact on surface water quality. pp 8-72. In R.Lal & B.A. Stewart (eds.) *Soil Processes and Water Quality*. CRC Press, Boca Raton, FL.
- Sharpley, A.N., & S. Rekolainen. 1997. Phosphorus in agriculture and its environmental implication. In Tunney, H., O.T. Carton, P.C. Brookes, & A.E. Johnston (eds.) *Phosphorus Loss from Soil to Water*. CAB International, New York.
- Sharpley, A. N., S.J. Smith, B.A. Stewart, & A.C. Mathers. 1984. Forms of phosphorus in soils receiving cattle feedlot waste. *J. Environ. Qual.* 13:211-215.
- Sharpley, A.N., & J.K. Syers. 1979. Phosphorus inputs into a stream draining an agricultural watershed: II. Amounts and relative significance of runoff types. *Water, Air and Soil Pollut.* 11:417-428.
- Sharpley, Andrew, T.C. Daniel, J.T. Sims, & D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. *J. Soil and Water Cons.* 51(2):160-166.
- Sibbesen, E., & A.N. Sharpley. 1997. Setting and justifying upper critical limits for phosphorus in soils. In Tunney, H., O.T. Carton, P.C. Brookes, & A.E. Johnston (eds.) *Phosphorus Loss from Soil to Water*. CAB International, New York.
- Simard, R.R., D. Vluis, G. Gangbazo, & S. Beauchemin. 1995. Phosphorus status of forest and agricultural soils from a watershed of high animal density. *J. Environ. Qual.* 24:1010-1017.
- Sims, J.T., & K.L. Gartley. 1996 *Nutrient management handbook for Delaware*. Coop. Bult. 59. Univ. of Delaware, Newark, DE.
- Sims, J.T., R.R. Simard, & B.C. Joren. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. *J. Environ. Qual.* 27:227-293.
- Sims, J. Thomas, Steve Hodges, & Jessica Davis. 1998. Soil testing for phosphorus: current status and uses in nutrient management program. In Sims, J. Thomas (ed.) *Soil Testing for Phosphorus: Environmental Uses and Implication*. SERA-IEG 17 USDA-CREES Regional Committee: Minimizing Agricultural Phosphorus Losses for protection of the Water Resources. Bulletin No. 389.
- Sjoerd, E.A., T.M. van der Zee, & Willem H. Van Riemsduik. 1988. Model for long-term phosphate reaction kinetics in soil. *J. Environ. Qual.* 17:35-41.


- Soil Survey Staff. 1999. Soil Taxonomy: A basic system for soil classification for making and interpreting soil surveys, 1999. Agriculture hand book 436. U.S. Government Printing Office, Washington, DC.
- Staples, R. Charles, Robert S. Tervola, & Edwin C. French. 1997. Forage Production Practices by Dairy Producers in the Suwannee Valley. Gainesville: Cooperative Extension Service, Institute of Food and Agriculture Science, Univ. of Florida. Circular 1049.
- Sweeten, J.M., M.L. Wolfe, E.S. Chasteen, M. Sanderson, B.A. Auvermann, & G.D. Alston. 1995. Dairy lagoon effluent irrigation: Effect on runoff quality, soil chemistry, and forage yield. P. 99-106. In K. Steele(ed.) Animal waste and the land-water interface. Lewis Publishers-CRC, New York.
- Thomann, R.V., & J.A. Mueller. 1987. Principles of surface water quality modeling and control. Harper Collins Publ., New York.
- Tiessen, H., and J.O. Moir. 1993. Characterization of available P by sequential extraction p.75-86. In M.R. Carter (ed.) Soil sampling and method of analysis. Can. Soc. Soil Sci. Lewis Publishers. Boca Raton, FL.
- Tisdale, Samuel L., Werner L. Nelson, James D. Beaton, & John L. Havlin. 1993. Soil Fertility and Fertilizers. 5th ed. Macmillan Publishing Company, New York.
- U.S. Environmental Protection agency (USEPA). 1996. Environmental indicators of water quality in the United states. EPA 841-R-96-002. USEPA Office of Water (4503F), U.S. Government Printing Office, Washington, DC.
- U.S. Environmental Protection Agency, 1988. Nonpoint source pollution in the US: report to Congress. Office of Water, Criteria and Standards division, USEPA, Washington, DC.
- Van Der Zee, S.E.A.T.M., & W.H. van Riemsdijk. 1991. Model for the reaction kinetics of phosphate with oxides and soils. In G.H. Bolt, M.F. DeBoodt, M.H.B. Hayes, & M.B. McBride (eds.), Interaction at the Soil Colloid-Soil solution Interface. Kluwer Academic Publ., Dordrecht. pp.205-239.
- Van Der Zee, S.E.A.T.M., L.G.J. Fokkink, & W.H. van Riemsdijk. 1987. A new technique for assessment of reversibly adsorbed phosphate. Soil Sci. Soc. Am. J. 51:599-604.
- Van Horn, H.H., A.C. Wilkie, W.J. Powers, & R.A. Nordstedt. 1994. Components of dairy manure management systems. J. Dairy Sci. 77:2008-2030.

- Van Horn, H.H., G.L. Newton, R.A. Nordstedt, E.C. French, G. Kidder, D.A. Graetz, & C.F. Chambliss. 1998. Dairy manure management: strategies for recycling nutrients to recover fertilizer value and avoid environmental pollution. Cooperative Extension Service, Institute of Food and Agriculture Science, Univ. of Florida. Circular 1016.
- Wang, H.D., W.G. Harris, & K.R. Reddy. 1992. Stability of P forms in dairy-influenced soils under leaching conditions. P.63. In Agronomy abstract. ASA, Madison, WI.
- Wang, H.D., W.G. Harris & K.R. Reddy. 1995. Stability of P forms in dairy-impacted soils under simulated leaching. *Ecol. Eng.* 5:209-227.
- Williams, J.D.H., J.K. Syers, & T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. *Soil Sci. Soc. Am. Proc.* 31:736-739.
- Wolfinger, R. D. and M.Chang, 1996. Comparing the SAS GLM and MIXED procedure for Repeated Measures. SAS institute Inc., Cary, NC.
- Woodard, K. R., E.C. French, D.A. Graetz, L.E. Sollenberger, L.A. Sweat, B.L. Wade, S.J. Rymph, B. Macoon, G.M. Prine, and H.H. Van Horn. 2000. Utilization of dairy waste effluent in year-round cropping systems for nutrient recovery and water quality enhancement. (In press).
- Yuan, T.L., & Dawn E. Lucas. 1982. Retention of phosphorus by sandy soils as evaluated by adsorption isotherms. *Florida Agr. Expt. Stas. Jour. Ser. No.* 3136.
- Zhang, T.Q., & A.F. Mackenzie. 1997. Changes in soil phosphorus fractions under long-term corn monoculture. *Soil Sci. Am. J.* 61:485-493.

BIOGRAPHICAL SKETCH

Abdullah Alshankiti was born on February 13, 1956, in Alqunfodah, Saudi Arabia. He completed his elementary school in his hometown of Alqunfodah. He moved to Riyadh, Saudi Arabia, to finish high school, and in 1979 he received a bachelor of science degree in agriculture from Riyadh University. In the same year, he joined the Department of Soil and Irrigation at the National Agriculture and Water Research Center, Riyadh, as a research assistant. In 1989, he obtained a Master of Science in Agriculture degree from California State University, Chico, and returned to work at the National Agriculture and Water Research Center, Riyadh. After earning his doctoral degree in soil and water science from the University of Florida in May 2000, he will return to his job at the National Agriculture and Water Research Center, Riyadh, Saudi Arabia.

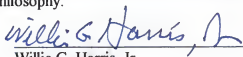
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Donald A. Graetz, Chair
Professor of Soil and Water Science


I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


R. Dean Rhue
Professor of Soil and Water Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

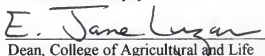

Willie G. Harris, Jr.
Professor of Soil and Water Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Roger A. Nordstedt
Professor of Agricultural and Biological Engineering

This dissertation was submitted to the Graduate Faculty of the College of Agricultural and Life Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 2000


E. Jane Lujan
Dean, College of Agricultural and Life Sciences

Dean, Graduate School



19461

UNIVERSITY OF FLORIDA



3 1262 08555 1660